THE CONSTITUTION OF SLAGS CONTAINING PHOSPHORUS PENTOXIDE IN FERROUS METALLURGY

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for the Degree of Doctor of Philosophy

by

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CONTENTS.

Part II - Slag-Metal Reactions.

INTRODUCTION.

In steelmaking, the removal of phosphorus from metal to slag occurs by oxidation and the subsequent formation of phosphates in the slag. To achieve a reasonable degree of dephosphorisation the slag must contain substantial quantities of lime, and if insufficient lime is present, rephosphorisation of the metal may occur at a later stage. Since phosphorus can only be removed by a basic slag, the permissible steelmaking processes are limited to those in which a dolomite or magnesite lining is used, i.e., basic processes. In the basic open hearth and electric furnace processes the phosphorus is largely removed at an early stage in the process. Basic Bessemer steelmaking is unique in that phosphorus removal cannot proceed before carbon and silicon have been eliminated from the metal, because of the presence of an acid slag of low oxygen potential in the early stages of the blow. On further blowing a more oxidising and basic slag is produced which can assist dephosphorisation. It is during this period in the process that the concentrations of ferrous oxide, lime and phosphorus pentoxide change most rapidly and consequently the melting characteristics of the ternary system formed by these three oxides are of greatest interest. Since this system is applicable mainly to the Basic Bessemer, little interest has been shown in it by British and American workers, as this method of steelmaking is practised only to a limited extent outside Europe.

Although many comprehensive studies of slag-metal relationships have been carried out, most of them have dealt with equilibria not primarily concerned with phosphorus removal, and little work has been

carried out on the equilibrium between molten iron and slags of the $CaO-FeO-P_2O_5$ system. Investigations of the phosphorus equilibrium between slag and metal have been mainly carried out using more complex slags, and considerable difficulty has been encountered in the interpretation of the data obtained. It was, therefore, decided in the present work to extend existing knowledge of the phosphorus equilibrium between molten iron and slags consisting mainly of lime, ferrous-oxide and phosphorus pentoxide. This slag-metal work required a previous knowledge of the $CaO-FeO-P_2O_5$ ternary system. Only a few results obtained by German workers are available on the mode of freezing and room temperature phase distribution in this system. It is probable that the practical difficulties encountered in such an investigation are mainly responsible for the present sparsity of data. Thus, the volatility of phosphorus pentoxide reduces the explorable region of the system. The highly refractory nature of lime demands a high temperature technique. The tendency to ferrite formation, particularly in highly basic slags also renders more difficult the interpretation of the results obtained. Nevertheless, the system was regarded as of sufficient importance to warrant further study. Part I of the present work will therefore describe work carried out in the $CaO-FeO-P_2O_5$ system and Part II will deal with slag-metal equilibrium work in which slags belonging essentially to this system were used.

PART I.

THE TERNARY SYSTEM CaO-FeO-P_2O_5.

CHAPTER I.

Review of the previous work on the constitution of the ternary system, $CaO-FeO-P_2O_5$.

In this review, the literature dealing with the associated binary systems will be dealt with, before the ternary system.

1. The System, Ferrous Oxide-Phosphorus Pentoxide.

One of the earliest investigations of this system (strictly speaking, the Fe-P-O system) was that of Kanz, Scheil and Schultz(1). Their slags were made from an iron-oxygen alloy containing 13 per cent oxygen, ferrophosphorus containing 26 per cent phosphorus and phosphorus pentoxide, and were melted in iron crucibles. They were unable to draw definite conclusions on the phase relationships from their results, but by combining them with those from the reduction experiments of Schenck(2), they concluded that iron was in equilibrium with $2FeO.P_2O_5$ and FeO.

A more thorough investigation of the binary join, ferrous oxide-phosphorus pentoxide, has since been made by Wentrup(3), whose melts were made in platinum crucibles in an atmosphere of purified nitrogen from powdered iron, ferric oxide and ferrous orthophosphate. Thermal and microscopic examination indicated the presence of one compound, $3FeO.P_2O_5$, which melted congruently at 1232°C. A eutectic between this compound and ferrous oxide was reported to occur at 30 per cent phosphorus pentoxide and 1008°C. The shape of the liquidus curve suggested by Wentrup is shown in Fig.1. The thermal arrest obtained at 942°C, was considered to represent an allotropic change in $3\ FeO.P_2O_5$. Some confirmation of this was obtained from microscopic examination of quenched specimens, which showed dark-grey crystals (α-$3FeO.P_2O_5$) below 942°C., but white laths or rhombic crystals (β-$3FeO.P_2O_5$) above this temperature.

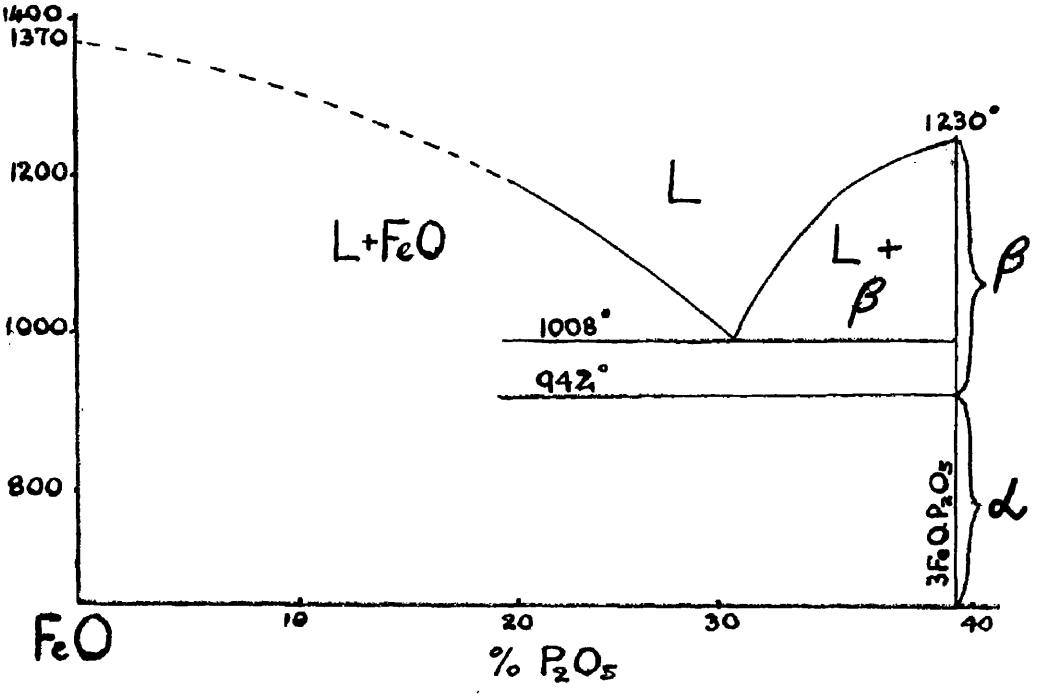

1400
1370
1200
1000
800
1230°
L
L+FeO
L +
β
β
1008°
942°
3FeO.P2O5
α
FeO
10
20
30
40
% P2O5

FIG. 1.

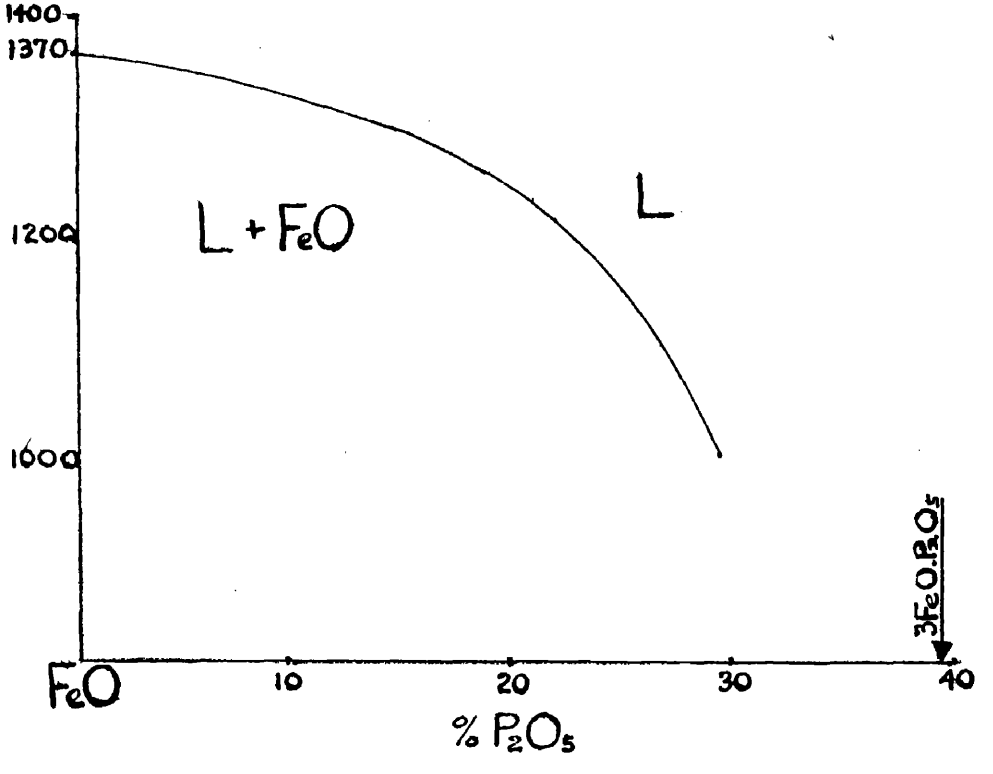

1400
1370
1200
1000
L + FeO
L
3FeO.P2O5
FeO
10
20
30
40
% P2O5

FIG. 2.

To the left of the eutectic composition, Wentrup noted the apparent presence of two primary phases, one white and the other grey in colour. Quenching from 1400°C, however, showed that the grey crystals were primarily formed, being partly superimposed by small metallic looking white dendrites. The grey phase was assumed to be ferrous oxide, some of which had decomposed to form magnetite and small dendrites of iron, as had been reported earlier by Pfeil(4).

More recently, Oelsen and Kremer (5), using iron crucibles, studied the shape of the ferrous oxide liquidus curve. It was suggested from the flat nature of their curve, shown in Fig.2, that there was a tendency to phase decomposition in the liquid state, in the ferrous oxide - $3FeO.P_2O_5$ system.

2. The System Ferrous Oxide-Calcium Oxide.

Ferrous oxide and calcium oxide show only a limited solubility in one another in the solid state. When melting occurs, considerable dissociation occurs and the system can no longer be regarded as a simple binary one. The reduction experiments of Schenck and co-workers(2), suggested that even in the solid state, ferrous oxide and calcium oxide did not form a quasi-binary section, because of the formation of ferrites (e.g., $2CaO.Fe_2O_3$) and ferro-ferrites. These results were confirmed by Kanz and co-workers(1), from a microscopic examination of ferrous oxide-calcium oxide mixtures melted in iron crucibles.

A more comprehensive study of the system was carried out by Hay and White(6) who confirmed that lime and ferrous oxide could not co-exist in the solid state, and the phase relationships advanced by them are shown in Fig.3. Hay and White suggested that in the presence of a strong base such as lime, ferrous oxide underwent self-oxidation to produce ferric oxide, and iron - the former then producing dicalcium ferrite,

$$3FeO + 2CaO \longrightarrow 2CaO.Fe_2O_3 + Fe$$

As a result of his investigations, however, Crook(7) rejected this view on the grounds that the metallic iron produced did not increase regularly with the lime content of the melts. He, therefore, treated the system as a binary one, but in order to explain the absence of free lime in certain slags, he postulated the existence of tricalcium ferrite, which in turn formed a binary join with ferrous oxide. He was unable, however, to identify this ferrite under the microscope, and its co-existence with ferrous oxide is therefore doubtful. The phase relationships advanced by Hay and White provide a more satisfactory explanation of Crook's data and must be regarded as the more reliable.

Hay and White also showed that additions of lime to ferrous oxide in platinum crucibles produced a marked drop in the melting point of ferrous oxide, which was subsequently followed by a rise in melting temperature at higher lime contents. These observations were confirmed later by Oelsen and co-workers(8), who melted ferrous oxide - lime mixtures in iron crucibles.

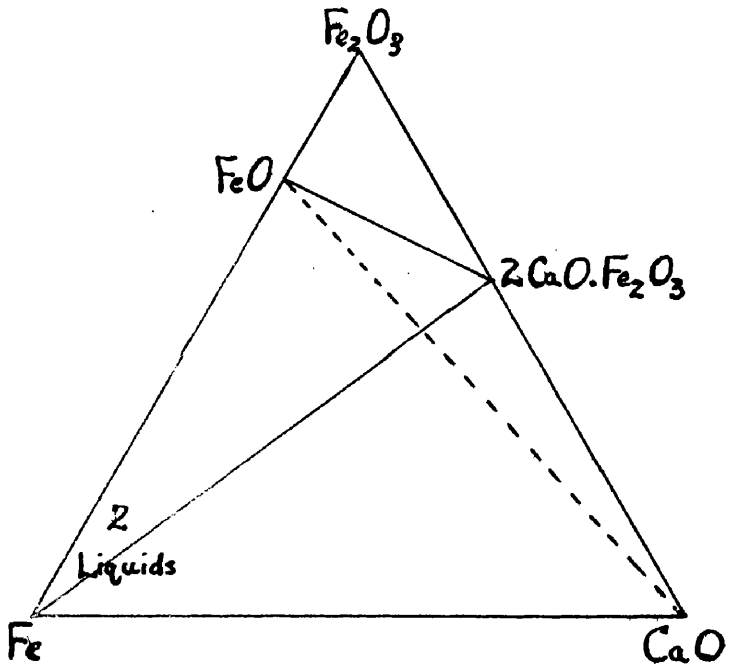


FIG. 3.

3. The System Calcium Oxide-Phosphorus Pentoxide.

Fig.4 shows part of the calcium oxide-phosphorus pentoxide thermal equilibrium diagram proposed by Körber and Trömel(9,10). In the composition range studied, four compounds were found to exist, two of which ($3CaO.P_2O_5$ and $4CaO.P_2O_5$) underwent polymorphic changes on cooling. Slag compositions containing more than 50 per cent lime have also been studied by Behrendt and Wentrup(11). The general shape of their diagram agrees substantially with that of Körber and Trömel(9,10), although the melting points of $3CaO.P_2O_5$ and $4CaO.P_2O_5$ (reported as 1790 and 1770°C respectively) are slightly higher than those shown in Fig.4.

It had been suggested by earlier workers(12) that the slow cooling of $4CaO.P_2O_5$ produced oxyapatite, $CaO.3(3CaO.P_2O_5)$ and that this compound should occur as a phase in the lime-phosphorus pentoxide system. However, neither Trömel(10) nor Behrendt and Wentrup(11) were able to detect the presence of this phase by X-rays in the above mentioned system. Bredig, Franck and Fuldner(13) have since shown that pure oxyapatite does not exist, but claim to have obtained a solid solution of oxy- and hydroxy-apatite ($Ca(OH)_2.3(3CaO.P_2O_5)$), containing approximately 65 per cent of the former.

4. The "Ternary" System, Calcium Oxide-Ferrous Oxide-Phosphorus Pentoxide.

Few results have been published on the phase relationships and the nature of the liquidus surface in this system. Körber and Oelsen(14), used somewhat incomplete data on the relevant binary systems, along with some complementary investigations to derive an approximate liquidus

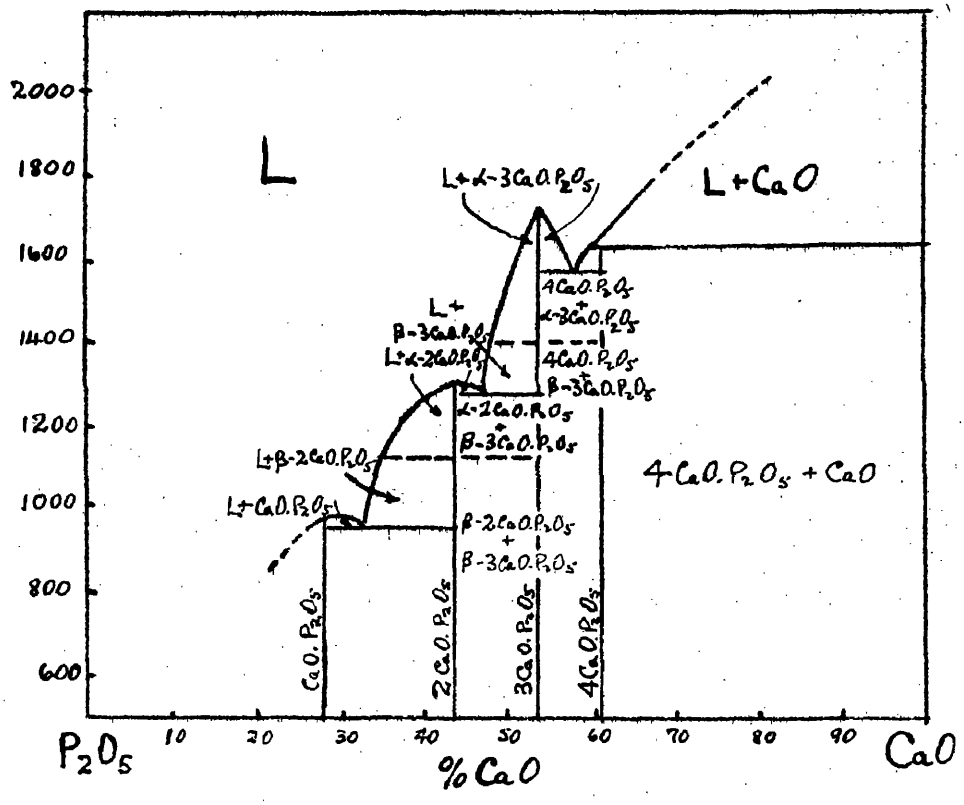

2000
1800
1600
1400
1200
1000
800
600
L
L+α-3CaO.P2O5
L+CaO
4CaO.P2O5
α-3CaO.P2O5
L+
β-3CaO.P2O5
4CaO.P2O5
L+α-2CaO.P2O5
β-3CaO.P2O5
α-2CaO.P2O5
β-3CaO.P2O5
L+β-2CaO.P2O5
4CaO.P2O5 + CaO
L+CaO.P2O5
β-2CaO.P2O5
+
β-3CaO.P2O5
CaO.P2O5
2CaO.P2O5
3CaO.P2O5
4CaO.P2O5
P2O5
10
20
30
40
50
60
70
80
90
CaO
%CaO

FIG. 4.

surface, as shown in Fig.5, which they applied to a discussion of the reactions taking place in the basic Bessemer process. A characteristic feature of their diagram was the solubility curve of the orthophosphate (abc at 1600°C), which stretched like a tongue towards the ferrous oxide corner. This form of isotherm was assumed because of the high congruent melting point of $3CaO.P_2O_5$, and from the observation that the melting point of ferrous oxide was depressed greatly by the addition of lime, and to a lesser extent by phosphorus pentoxide.

In a recent paper Oelsen and Maetz(15) reported that, when additions of tricalcium phosphate or dicalcium phosphate were made to ferrous oxide melts (in iron crucibles), only a very small proportion dissolved at 1450°C - the bulk remaining suspended as a hard crust in the upper part of the melt. Further work showed the bottom layer to be composed almost entirely of ferrous oxide, while the top layer contained large amounts of lime and phosphorus pentoxide, in association with some ferrous oxide. It can be seen in Figure 6, that the area of immiscibility so produced, extended from the ferrous oxide corner towards a composition midway between $3CaO.P_2O_5$ and $4CaO.P_2O_5$. From the direction of the tie lines they concluded that the section, ferrous oxide - $3CaO.P_2O_5$ was a quasi-binary, but were unable to prove it, as their investigation was limited by the melting point of the iron crucibles.

Since no regions of immiscibility were present in the binary systems, it was clear that the immiscibility gap must lie within the ternary system. Similar results were obtained in an investigation(15) of the effect of calcium fluoride additions to lime-ferrous oxide mixtures, as

FIG. 5.

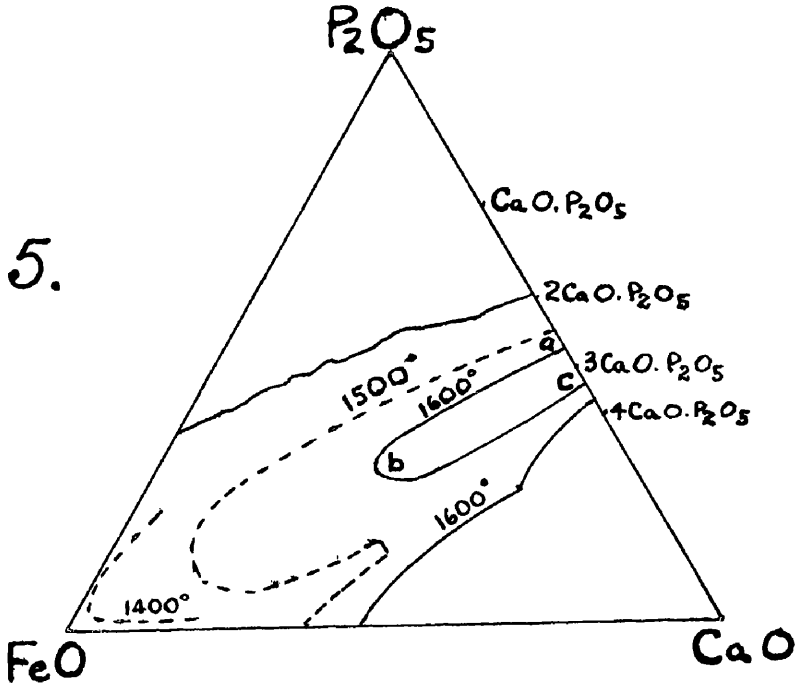
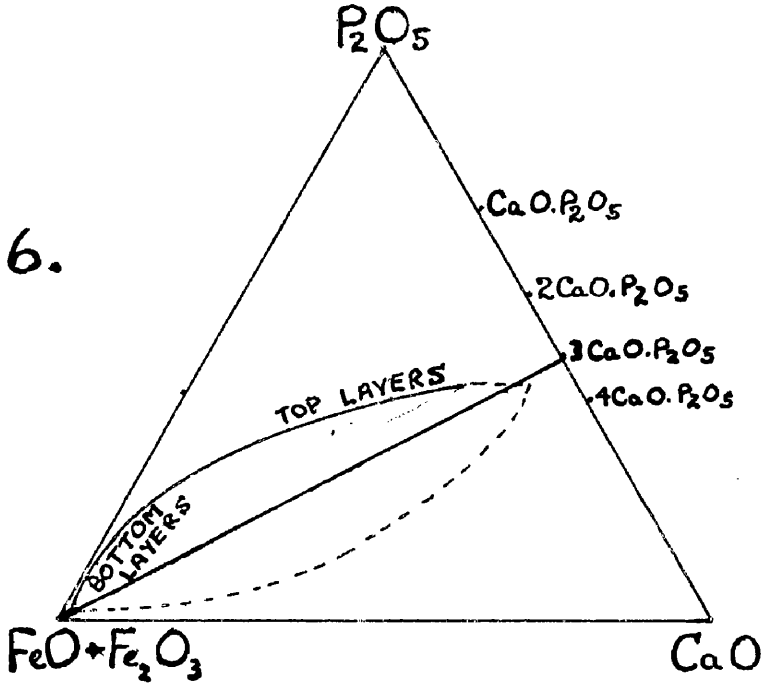

P2O5
CaO.P2O5
2CaO.P2O5
3CaO.P2O5
4CaO.P2O5
a
c
b
1500°
1600°
1600°
1400°
FeO
CaO

FIG. 6.


P2O5
CaO.P2O5
2CaO.P2O5
3CaO.P2O5
4CaO.P2O5
TOP LAYERS
BOTTOM LAYERS
FeO+Fe2O3
CaO

shown in Fig.7. $3CaO.P_2O_5$ was considered to show the same behaviour as calcium fluoride with respect to mixtures of lime and ferrous oxide, and on this assumption the immiscibility boundary at temperatures greater than 1480°C was predicted in the phosphate ternary system. This is shown by the dotted line in Fig.6.

Later, in collaboration with the above workers, Trömel(10) investigated this region using rhodium crucibles. Because of the expense of rhodium, the technique employed, differed from that practiced by Oelsen and Maetz, in which the slag was sampled after breaking up the crucible. In contrast Trömel isolated the top layer (at a temperature above its melting point) by successively dipping a cold rhodium rod into it, and removing the chilled slag. After separation was completed the bottom layer was poured from the crucible. The results obtained from these experiments confirmed the earlier prediction of Oelsen and Maetz.

White(16) has pointed out that in the quarternary system, lime-iron-ferric oxide-phosphorus pentoxide, the section, lime-ferrous oxide-phosphorus pentoxide, is not a true ternary, as it is partly over-lapped by the iron-liquid slag immiscibility zone. Also, with certain compositions near the "binary" section, ferrous oxide-lime, the separation of dicalcium ferrite from the melt was considered highly probable. White suggested that it might be significant that the region of immiscibility proposed by Oelsen and Maetz, occurred in the composition range where these above effects were most likely to be encountered. This may be partly true, but the reason for phase decomposition can be better

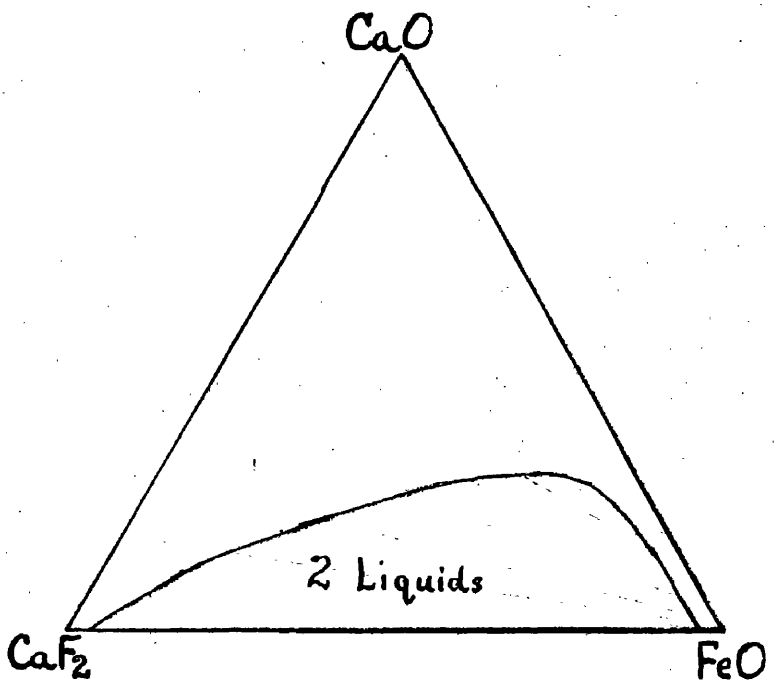


FIG. 7.

explained by considering the relative sizes of the ions present in the liquid slag. This will be dealt with more fully in Chapter 4.

CHAPTER 2.

Experimental Technique.

A. Preparation of Materials Used.

1. Ferrous Oxide. A steel container was filled with ferrous oxalate, placed in a steel tube and heated under vacuum in a horizontal nichrome wound furnace. The temperature was raised to 200°C and held therefor half an hour to remove moisture from the powder. The tube was then heated to 700°C, during which time the evolved gases were removed. After remaining at 700°C for half an hour, the temperature was increased to 1000°C in order to sinter the material, and so present the minimum surface area to oxidation. The tube was then removed and quenched in water. When cold, the powder was tested with a magnet, analysed for iron and stored under vacuum. Analysis showed the product to contain one per cent of oxygen in excess of that corresponding to the formula, FeO.

2. Calcium Oxide. This was prepared by the calcination of "analar" calcium carbonate at 1000°C.

3. Phosphorus Pentoxide. May and Baker phosphorus pentoxide containing less than 0.05 per cent insoluble matter was used.

4. Calcium Orthophosphate. This was prepared by heating very slowly to 1000°C, the correct proportions of lime and phosphorus pentoxide. A little of the latter was lost due to volatilisation but all samples were subsequently analysed.

B. Preparation of Crucibles.

Slags, whose melting points were below 1470°C, were melted in mild steel crucibles. These were made by drilling a 3/4 inch diameter hole to a depth of 1.5 inches, in a solid piece of one inch diameter mild steel bar.

For slags which melted over 1470°C, mild steel could not be used with safety, and therefore molybdenum and magnesia crucibles were substituted.

Molybdenum crucibles were made from 1/2 inch diameter rod, while in the production of magnesia crucibles, capable of retaining ferrous oxide slag at steelmaking temperatures, two possible methods were investigated - one using induction heating and the other using slip-casting.

1. Induction Heating. Dancy(17) claimed to have produced m agnesia ware by fusing magnesia powder, using an induction heated graphite core and it was hoped to produce by this method, a crucible with a fused internal layer which would be inpervious to liquid slags.

Fused magnesia powder (50 mesh) was packed round a graphite core, and heated in an induction coil. It was found that long heating periods produced a thick sintered crucible, while more rapid heating gave rise to a thinner wall with a more glazed internal surface. Glazing was discontinuous, however, and was confined to isolated groups of grains, giving rise to highly permeable crucibles. During heating, reduction of the magnesia occurred, according to the equation,

$$MgO + C \longrightarrow CO + Mg$$

and since this reaction proceeds at temperatures over 1970°C, it is probable that the magnesia was completely reduced before its melting point was reached. For this reason, this method was considered incapable of producing crucibles suitable for the present investigation, and attention was therefore turned to the possibility of making slip-cast crucibles.

2. Slip-Casting. This consisted of grinding the fused magnesia in a steel ball mill for twenty four hours, deflocculating the particles in a suitable medium, and casting into a plaster of Paris mould. As a deflocculant, ten per cent hydrochloric acid was first used, but this was found to be unsatisfactory as the crucibles cracked severely on drying in the mould. On substituting commercial ethanol for hydrochloric acid, cracking in the green state was eliminated, but the crucibles were more liable to stick to the mould. This difficulty was overcome by imparting a slight taper to the mould and by dusting it with French chalk, before pouring in the slip. Crucibles produced in this way dried successfully, but showed considerable cracking when fired to 1550°C. Ethanol, dried with quicklime gave, in some cases a sound crucible on firing, but not in others.

It soon became apparent that the cracking tendency was governed by the presence of magnesium hydroxide, which on firing, dehydrated and so produced a change in volume. Ethanol, dried by the Grignard method, was therefore used, when all crucibles fired without cracking. These crucibles were exceptionally strong, (physically) dense and very impervious.

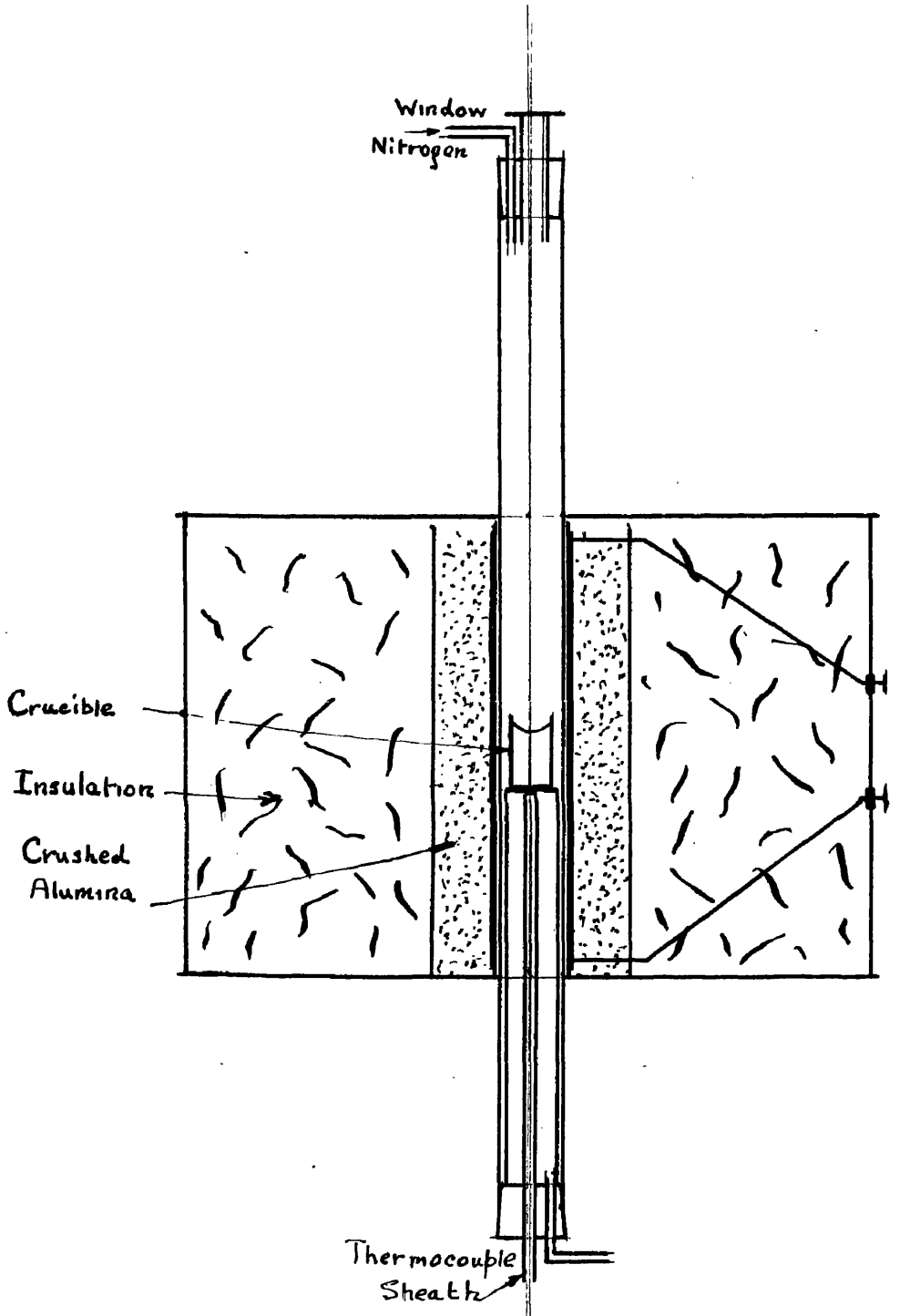

Window
Nitrogen
Crucible
Insulation
Crushed
Alumina
Thermocouple
Sheath

FIG. 8.

The slag picked up magnesia by solution from the surface of the crucible, but in most cases, no penetration occurred.

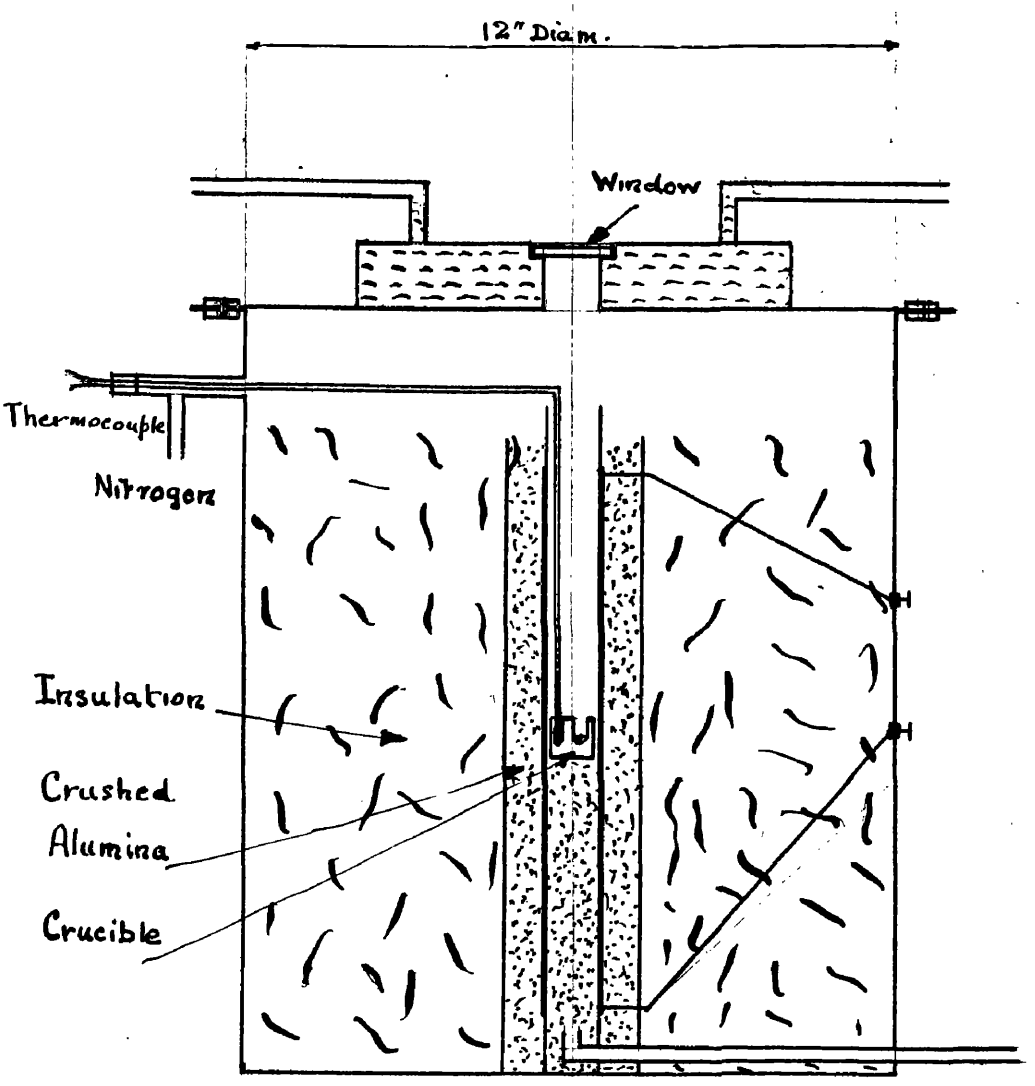
C. Melting Technique.

In the investigation of the binary system, ferrous oxide-phosphorus pentoxide, both oxides were used as starting materials. Because of the hygroscopic nature of phosphorus pentoxide, weighing and mixing of the constituents were carried out in a weighing bottle, after which the charge was quickly transferred to the crucible.

In the case of ternary slags, phosphorus pentoxide was added wherever possible, as a calcium phosphate of predetermined composition, thus eliminating the use of a weighing bottle. The starting materials were ground, intimately mixed in a mechanical agate mortar and pressed into pellets, before being added to the crucible.

Melting experiments were carried out in a platinum wound resistance furnace of standard design, as is shown in Fig.8. To prevent oxidation of the crucible and contents during melting, an atmosphere of purified nitrogen was maintained in the furnace tube. This was prepared by removing the oxygen from commercial nitrogen by passing it successively over copper gauze, iron turnings and manganese at 700°C., and finally over magnesium turnings at 450°C.

The purified nitrogen was then introduced at the top of the furnace tube, and the issuing gas at the bottom was bubbled through water such that the flow rate could be observed. This arrangement eliminated the "chimney effect" and also served to maintain a slight positive pressure inside the tube.


12" Diam.
Window
Thermocouple
Nitrogen
Insulation
Crushed
Alumina
Crucible

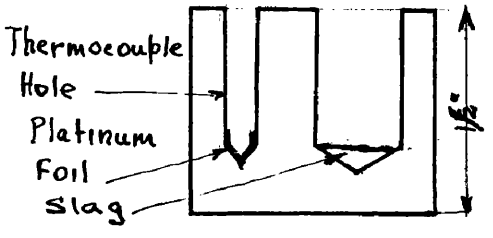

Thermocouple
Hole
Platinum
Foil
Slag

FIG. 9.

Temperature measurements were made, using a platinum 13 per cent rhodium, platinum-rhodium thermocouple, which was located at the base of the crucible and protected from the furnace atmosphere by a mullite sheath.

The behaviour of the charge during melting was observed through a glass window in the top bung. Prior to cooling in the furnace, each slag was kept molten for half an hour to ensure homogeneity. When cold, the crucible was removed and sectioned longitudinally - one half being retained for microscopic examination and the other for chemical analysis and melting point determination.

D. Melting Point Determination.

Throughout the investigation two methods were used. One relied on the visual observation of the beginning and end of melting, while the other was based on thermal analysis.

The apparatus used in the first-mentioned method is shown in Fig.9, and consisted of a small platinum wound resistance furnace which was placed vertically at the centre of a gas-tight steel case. The top consisted of a water-cooled lid, at the centre of which was located a quartz window. Both lid and case were firmly bolted together, and the junction made gas-tight by placing a layer of asbestos paper between the bearing surfaces. Of the two side tubes shown, one served the dual rôle of supplying nitrogen to the furnace and the insertion of the thermocouple, while the other provided an outlet for the nitrogen.

The crucibles used (Fig.9), were made from 5/8 inch diameter mild steel bar, cut to the required length and bored to a depth of 1/4 inch at one end. A special small hole to accommodate the end of the thermocouple was drilled alongside, care being taken to ensure the same depth of slag and thermocouple tip. Contamination of the thermocouple junction by the iron was prevented by surrounding the junction with platinum foil. In order to record the exact temperature the distance between the central hole and the couple was made as small as possible. This precaution was necessary, due to the unavoidable temperature gradient set up in such a small furnace.

The slags whose melting points were to be determined, were crushed and heated in an atmosphere of purified nitrogen. Fine powder showed more clearly the beginning of melting but not the end, whereas for large particles the reverse was true. Any change in position of the particles was taken as the beginning of melting, while the particles after complete melting, showed a smooth flat surface in the crucible. The melting points of silver foil (961°C) and fayalite($2FeO.SiO_2$)(1205°C) were used to check the accuracy of the method. The values obtained were 960°C and 1200°C respectively, i.e., within 5°C of the published values.

Because of the strong creeping tendency of the slags examined, however, this method was not completely satisfactory and had to be replaced by one relying on the thermal changes on heating and cooling.

In this method, a platinum-platinum rhodium thermocouple was placed inside a thin walled, 1/4 inch diameter mild steel sheath, and surrounded by the preformed slag in a one inch diameter mild steel crucible. Iron contamination of the couple was prevented by placing a piece of platinum foil at the bottom of the sheath. Heating was again carried out in an atmosphere of purified nitrogen.

During heating, the time required for the temperature to rise by 0.1 millivolts on the potentiometer was recorded, but because of the tendency to supercooling shown by the slags, on cooling, the temperature was noted every 30 seconds. When supercooling occurred, the highest temperature reached when freezing took place was assumed to be the end of freezing. In the case of the slags which could not be melted in mild steel crucibles, magnesia crucibles and a similar sheath of molybdenum were substituted.

Similar duplicate determinations carried out on fayalite and on the fayalite-FeO-eutectic (m.p. 1177°C) gave melting points at 1200°C, 1202°C and 1173°C, 1180°C respectively, again indicating an experimental error of $\pm$ 5°C.

CHAPTER 3.

Experimental Investigation of the Binary System Ferrous Oxide - Phosphorus Pentoxide.

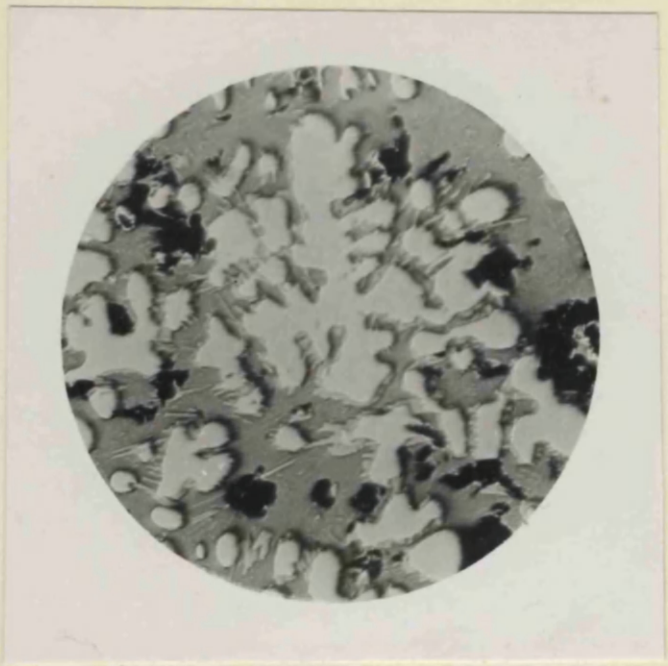
A series of slags, ranging from pure ferrous oxide to 38.4 per cent phosphorus pentoxide - 61.6 per cent ferrous oxide, was melted and cooled in the furnace, at a rate of 120 degrees per hour. Visual inspection showed all the slags to be homogeneous and black in colour.

1. Microscopic Examination.

Micro 1, which is typical of slags of high ferrous oxide content, shows large white dendrites of ferrous oxide in a eutectic matrix of ferrous oxide (light needles) and ferrous orthophosphate (grey). As the ferrous oxide content was decreased, the amount of eutectic increased at the expense of the primary crystals. Micro 2, shows a structure which is almost entirely composed of eutectic, with a slight amount of ferrous orthophosphate in excess of the eutectic composition. On decreasing the ferrous oxide content further, the amount of primary ferrous orthophosphate increased, as can be seen in Micro 3, which corresponded to a slag containing 38.4 per cent phosphorus pentoxide. In this photograph, it is of interest to note the distinct lath-like appearance shown by ferrous orthophosphate when present in large quantities. No trace of ferrous orthophosphate in the β form, described by Wentrup(3) was detected, even after quenching from 900°C.

Despite numerous attempts, it was not possible to melt ferrous orthophosphate, without an excess of ferrous oxide associated with it. The maximum phosphorus pentoxide content obtained, by melting mixtures of ferrous oxide and phosphorus pentoxide, was a slag containing 34.6 per cent phosphorus pentoxide, which compared with a maximum value

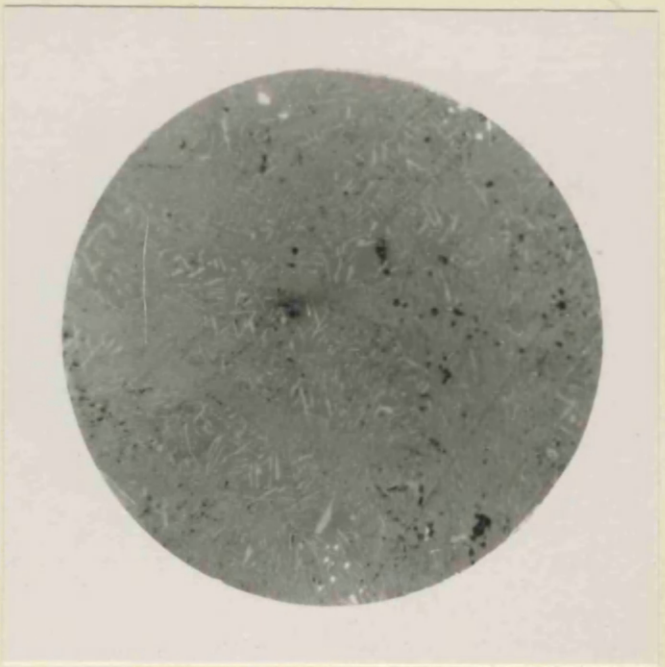
1



81% FeO, 5% Fe_2O_3, 14% P_2O_5

X100

2



63% FeO, 5% Fe_2O_3, 32% P_2O_5.

X250

UNETCHED.

3

58% FeO, 4% Fe_2O_3, 38% P_2O_5

X250

4

69% FeO, 3% Fe_2O_3, 27% P_2O_5

X250

UNETCHED.

of 30 per cent, reported by Kanz, Scheil and Schultz(1), in their experiments.

Sintering the correct proportions of both oxides, in a pure nitrogen atmosphere, prior to melting in an iron crucible, gave a slightly higher value of 36.5 per cent phosphorus pentoxide. In these experiments sintering was carried out in a crucible fitted with a tight cap, for 72 hours at 400°C, and then for a further 65 hours at 750°C. The "purest" ferrous orthophosphate was obtained, however, by melting a mixture of ferrous-oxide and ammonium hydrogen phosphate, which had been previously sintered at 900°C, for 12 hours. This gave a phosphorus pentoxide content as high as 38.4 per cent, but still corresponded to the presence of at least one percent excess ferrous oxide. Volatilisation of the phosphorus pentoxide must have occurred during melting as chemical analysis showed no loss to have occurred after sintering.

Further microscopic examination of slag compositions containing primary crystals of ferrous oxide, showed the presence of a third light grey phase, which occurred round the ferrous oxide dendrites, (as is shown in Micro 4) and resembled a reaction rim typical of a peritectic reaction. The existence of a peritectic in the system, however, seems unlikely as the amount of light grey phase remained roughly constant over all compositions in the primary ferrous oxide field. Hence, as the eutectic composition was approached there was an increase in the ratio of light grey phase to the amount of ferrous oxide present, as can be seen by comparing micros 1 and 4.

Wentrup(3) reported this light grey phase in his slag structures and attributed it to the breakdown of wüstite into iron and ferric oxide, although it was present even after quenching from 1400°C. This finding was in agreement with the earlier work of Kanz, Scheil and Schultz(1), and was also confirmed by similar experiments carried out from 600°C, in the present investigation. It is surprising that the decomposition of wüstite could not be prevented by rapid quenching, since this reaction has been reported to be very slow by Chaudron and Forestier(18). It would therefore seem, if the above explanation is accepted, that in the presence of ferrous orthophosphate, the breakdown is so strongly accelerated that it cannot be prevented by water quenching.

However, the binary system, ferrous oxide-phosphorus pentoxide, should strictly speaking, be treated as a ternary system, e.g., $Fe-Fe_2O_3-P_2O_5$ or Fe-P-O, on account of the instability of ferrous oxide, with respect to iron and its other oxides, and from a knowledge of such a ternary system it should be possible to explain the presence of this light grey phase, with certainty. Thus it is possible that the grey and white phases are Fe_3O_4 and FeO respectively.

2. Melting Point Determinations.

(a) Melting Point Furnace Method. Originally, the apparatus shown in Figure 9 was used for melting point determinations, but it was found to be unsuitable, on account of the very pronounced creeping tendency shown by iron phosphate slags. It is well known that phosphate slags in general are prone to this phenomenon, but the creeping of iron

phosphate slags in small iron crucibles was surprising because of its magnitude.

By this method, however, it was possible to determine the beginning of melting, after which the first liquid formed - presumably the eutectic composition, crept away from the remaining primary crystals. Thus, in the primary field of ferrous oxide the apparent end of melting always occurred at 1370°C, i.e., the melting point of ferrous oxide, and for slag compositions containing more than 30 per cent phosphorus pentoxide melting always appeared to end at about 995°C. This was taken as an approximate measure of the melting point of ferrous orthophosphate.

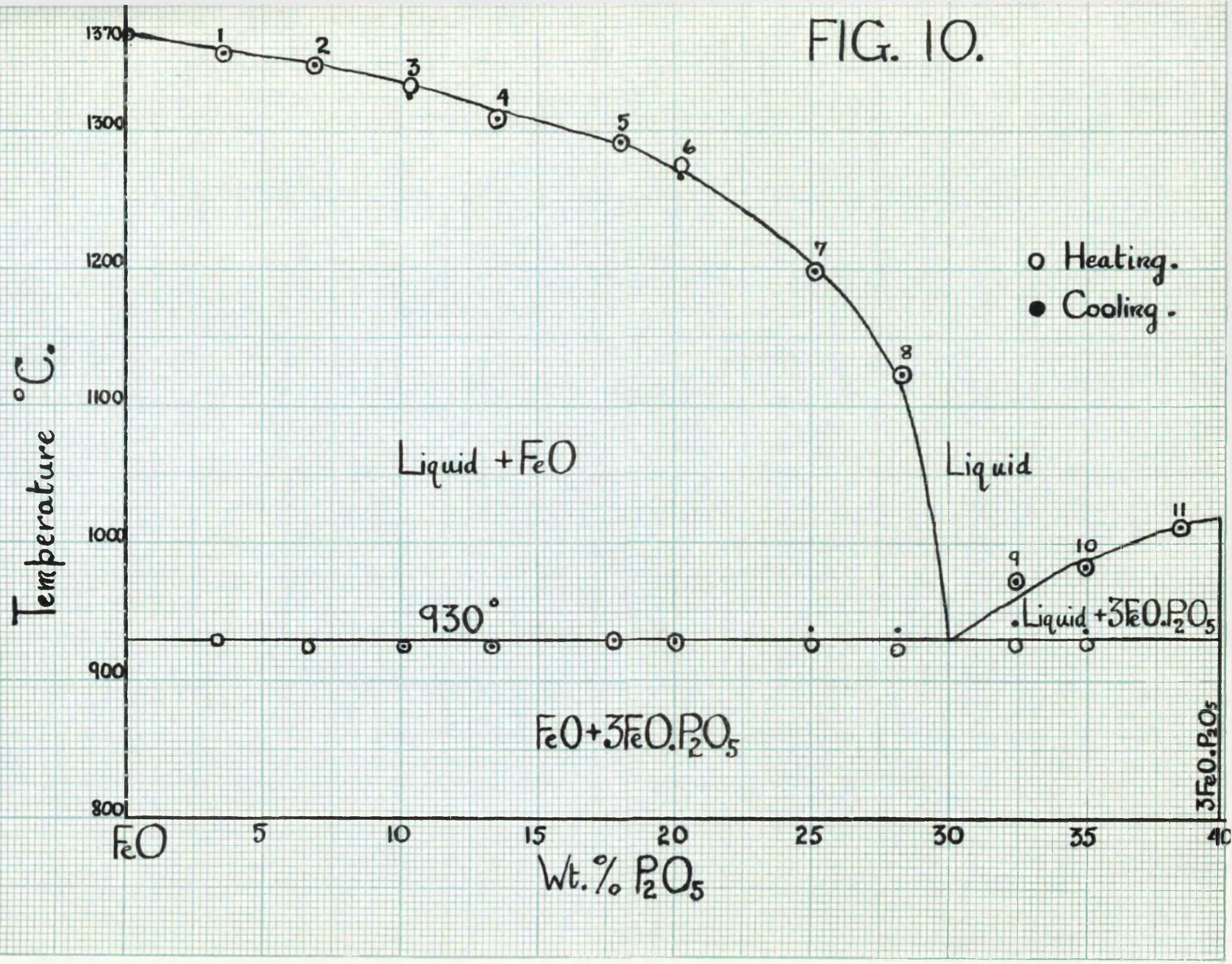
Since the true end of melting could not be determined by this method, it was decided to use a thermal analytical method. This is only applicable to substances which crystallise easily, and although Warren (19) has reported the existence of phosphate glasses, its application to iron phosphate slags was permissible as no glass formation was detected in the microscopic examinations.

(b) Thermal Analysis. The results of thermal analysis of slags in this system are shown in Table 1 and plotted in the thermal equilibrium diagram shown in Fig.10. It can be seen that the ferrous oxide-phosphorus pentoxide system shows one compound, ferrous orthophosphate ($3FeO.P_2O_5$) which melts congruently at 1020°C and gives rise to a eutectic with ferrous oxide at 930°C and 30.0 per cent phosphorus pentoxide.

TABLE I.

Slag	THERMAL ANALYSIS							Melting Point Furnace.	
	Composition			Heating		Cooling			
	FeO	Fe_2O_3	P_2O_5	1st Arrest °C	2nd Arrest °C	1st Arrest °C	2nd Arrest °C	Started Melting	Finished Melting.
1	89.1	7.5	3.2	930	1360	1360	-	N.D.	N.D.
2	88.2	5.5	6.5	925	1350	1350	-	N.D.	N.D.
3	83.5	6.7	10.0	925	1335	1330	925	940	1370
4	81.1	5.7	13.2	925	1312	1312	925	N.D.	N.D.
5	75.2	6.5	17.8	930	1295	1295	930	942	1370
6	75.2	5.2	20.0	930	1275	1270	930	942	1367
7	69.1	6.0	25.0	930	1200	1200	940	N.D.	N.D.
8	66.8	5.0	28.2	925	1125	1125	940	N.D.	N.D.
9	63.5	5.1	32.5	930	970	970	945	937	997
10	61.1	3.3	35.0	930	985	985	940	944	992
11	58.0	3.1	38.4	-	1015	1015	-	N.D.	N.D.

FIG. 10.


Temperature °C.
1370
1300
1200
1100
1000
900
800
1
2
3
4
5
6
7
8
9
10
11
o Heating.
• Cooling.
Liquid + FeO
Liquid
930°
Liquid + 3FeO.P2O5
FeO + 3FeO.P2O5
3FeO.P2O5
FeO
5
10
15
20
25
30
35
40
Wt. % P2O5

That the system is eutectiferous, is in agreement with Wentrup's diagram, but although the eutectic temperature has been found to be considerably lower, the eutectic composition is identical. Since pure ferrous orthophosphate could not be obtained it was only possible to estimate its melting point by producing the liquidus curve from the eutectic to a point corresponding to its composition, and the extrapolated value was found to be 1020°C. This compares with 1230°C reported by Wentrup(3) and is slightly higher than the value obtained in the melting point furnace.

Recently Pearson, Turkdogan and Fenn(20) have reported the melting point of manganese orthophosphate ($3MnO.P_2O_5$) to be 1119°C. A surprising feature of their technique was the use of alumina crucibles at temperatures which would have permitted the use of iron or even manganese containers, although it was claimed that no crucible attack occurred. Since the melting points of basic phosphates may be regarded as a measure of their stabilities, the melting point of ferrous orthophosphate would be expected to be similar or slightly lower than that of the orthophosphate of manganese. In the light of this argument the melting point of ferrous orthophosphate determined in this investigation, is in better agreement with theoretical considerations than the value of 1230°C obtained by Wentrup.

The melting point of ferrous oxide* was found to be 1370°C., and shows good agreement with values of 1367°C and 1380°C as determined by Carter and Ibrahim(21) and Bowen and Schairer(22) respectively.

* Wüstite melts incongruently with separation of iron and formation of a liquid slightly richer in oxygen then the original wustite.

The most interesting feature of the diagram shown, is the very flat nature of the liquidus curve between ferrous oxide and the eutectic composition and in this respect, the diagram shows a further deviation from that of Wentrup(3), although it should be noted that he predicted this section of the liquidus from rather incomplete data on the melting temperatures of the eutectic region. The anomalous shape of the curve, however, is in general agreement with the findings of Oelsen and Kremer(5).

In an endeavour to reduce to a minimum, the ferric oxide content of the melts, the liquid slag was superheated by as much as 150 to 200°C, or as far as the crucibles would allow, in the case of those slags rich in ferrous oxide. This proved successful when the P_2O_5 contents were low, but with higher contents, a vigorous boil developed, and it was found that the crucible walls showed appreciable attack, especially near the liquid surface. Metal was deposited at the base of the crucible and analysis of this, and the resultant slag, showed the metal to have gained phosphorus at the expense of the slag.

In order to determine the nature of the gas evolved during the boil, samples of the furnace atmosphere were drawn, but in all cases dilution by the nitrogen in the furnace tube was too great. The gas was collected over mercury, however, by leading it from the crucible through a silica tube, and on analysis, it was found to be absorbed by potassium hydroxide, and contained phosphorus.

The fact that it was gaseous at room temperature, eliminated the possibility of it being a known oxide of phosphorus; namely P_2O_5, P_2O_3, P_2O_4, P_4O. The possibility of a reaction involving the furnace atmosphere was also ruled out as the nitride P_3N_5 and the oxynitride PNO, are also solid at room temperature.

One other possibility suggested itself, namely, the presence of carbon dioxide and carbon monoxide, (formed by the oxidation of carbon from the mild steel crucibles, by the slag) associated with traces of phosphorus pentoxide (carried over from the crucible). It was found, however, that the gas was almost entirely absorbed by the strong alkali solution, which would suggest the presence of nearly pure carbon dioxide - the formation of which by the slag, was impossible as the oxygen potential of ferrous oxide is lower than that of carbon dioxide.

Thus the information known about this gas may be summarised as follows:-

(a) It could be formed from iron, carbon, phosphorus, oxygen and nitrogen.

(b) It was absorbed by strong alkali solution and therefore must be acidic in character.

(c) It contained phosphorus.

Unfortunately, time did not permit further investigation of this reaction, which was apparently not observed by previous investigators(1)(3), (although Oelsen and Kremer(5) reported porous slags), possibly because they did not superheat their slags to the extent practiced in this investigation.

CHAPTER 4.

Experimental Investigation of the Ternary System $CaO-FeO-P_2O_5$.

A. Iron Crucibles.

In the same way as mixtures of the binary system, ferrous oxide-phosphorus pentoxide were melted, two other series were produced in iron crucibles by adding 1 and 5 per cent lime respectively. In addition other ternary mixtures were similarly prepared.

(a) 1 per cent CaO Series. Microscopic examination of the slags in this series, showed structures identical with those of the corresponding ferrous oxide-phosphorus pentoxide ratio, in the binary system. Since no new phase could be detected, it can be inferred that lime was either present in solid solution with ferrous oxide, or combined with phosphorus pentoxide as a phosphate - probably tricalcium phosphate, which in turn was in solid solution with ferrous orthophosphate. Due to the very strong affinity shown by lime for phosphorus pentoxide the second possibility is considered the more probable.

(b) 5 per cent CaO Series. On examination of the slags in this series, some were found to show two immiscible layers. In order to minimise any change in layer compositions on cooling, these slags were cooled more rapidly than the other series. (A cooling rate of 300 to 400°C per hour was employed). Slags were polished and each layer subjected to chemical analysis, the results of which are shown in Table 2, and Figure 11.

It was found that the line of demarcation between top and bottom layers was very pronounced so that separation could be accomplished with comparative ease. Visual inspection showed the bottom layer to be black, with a metallic lustre, while the top layer was found to be lighter in

TABLE 2.

WEIGHT PER CENT.

Slag No.	Quenching Temp. °C.	Original Composition			Top Layer.					Bottom Layer.				
		FeO	P_2O_5	CaO	FeO	Fe_2O_3	CaO	MgO	P_2O_5	FeO	Fe_2O_3	CaO	MgO	P_2O_5
1	1360	80	15	5	57.1	3.1	10.2		30.0	84.1	7.5	2.0		7.0
2	1370	85	10	5	44.9	1.2	19.0		35.0	84.5	11.5	1.3		2.9
3	1370	74	16	10	34.5	1.6	27.6		36.0	87.1	8.3	1.1		4.1
4	1360	70	16	14	26.6	2.3	32.0		39.2	88.6	9.0	1.0		1.4
5	1400	68	16	16	23.0	1.6	34.0		39.8	89.5	7.0	1.4		2.0
6	1460	90	5	5	20.2	1.0	40.0		39.4	89.4	7.0	2.6		1.0
7	1540	50	23	27	10.1	1.0	43.5	3.3	42.1	67.0	21.0	8.0	3.7	0.6
8	1540	45	25	30	6.5	1.0	44.0	5.6	42.3	70.0	12.0	10.2	5.9	1.8
9	1560	50	20	30	8.0	1.0	45.5	3.0	42.0	58.0	17.3	16.1	5.5	1.7
10	1560	50	15	35	10.1	3.6	47.5	3.1	35.2	47.3	24.6	20.5	4.1	2.8
11	1520	45	16	39	23.5	4.1	44.5	2.3	25.3	36.0	21.0	30.6	4.7	8.0
12	1600	N.D.	N.D.	N.D.	9.8	N.D.	44.9	-	40.2	93.2	N.D.	3.4	-	0.55

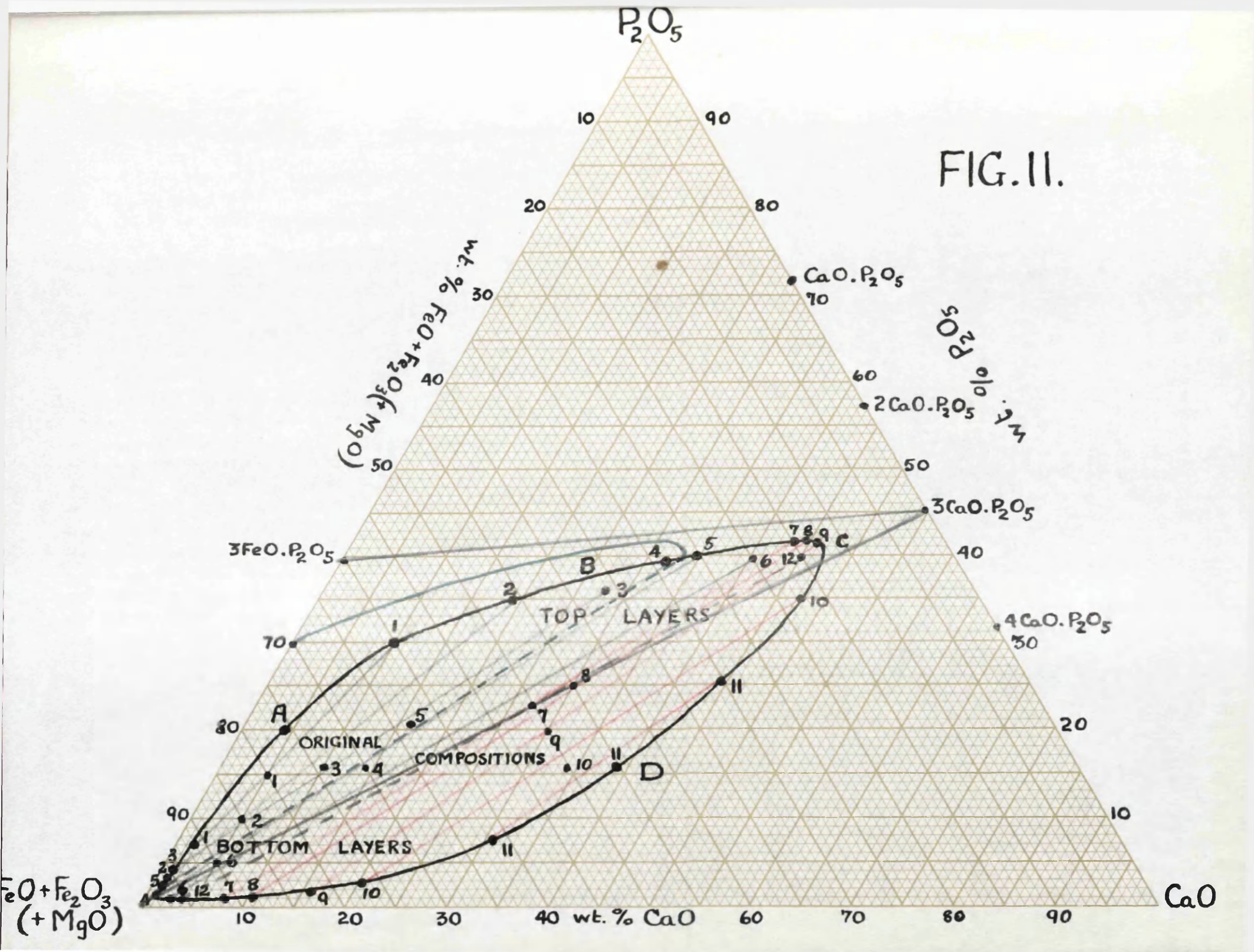


FIG. 11.
P_2O_5
$CaO.P_2O_5$
$2CaO.P_2O_5$
$3CaO.P_2O_5$
$4CaO.P_2O_5$
$3FeO.P_2O_5$
wt. % P_2O_5
wt. % $FeO+Fe_2O_3$ (+ MgO)
wt. % CaO
$FeO+Fe_2O_3$ (+ MgO)
CaO
A
B
C
D
TOP LAYERS
ORIGINAL COMPOSITIONS
BOTTOM LAYERS

colour, and less metallic in appearance. As the top layer became richer in lime and the corresponding bottom one more deficient in lime, the difference in the outward appearance of each layer became more marked - the top layer tended to assume a light grey colour in contrast to the more brilliant dark colour of the bottom layer.

B. Microscopic Examination.

(a) Bottom Layers. Microscopic examination of the bottom layers showed large primary dendrites of ferrous oxide, in a ferrous oxide-phosphate eutectic, i.e., structures similar to those encountered in the high ferrous oxide region of the ferrous oxide-phosphorus pentoxide binary system. Micro 5, shows the structure of the bottom layer of slag No.1. Here the white dendrites are ferrous oxide (accompanied by the associated grey phase, observed in the binary structures) and the dark background, eutectic.

It was found that as the layer compositions approached the ferrous oxide composition, the ratio of primary crystals of ferrous oxide to eutectic, increased accordingly. This becomes evident on comparing Micros. 5 and 6 - the latter showing the structure of the bottom layer of slag 4.

(b) Top Layers. When examined under the microscope some top layers showed a structure of primary phosphate and eutectic (slag No.8), while others showed small white dendrites of ferrous oxide (slag No.1) and eutectic. It was found that as the lime content increased the size and proportion of ferrous oxide dendrites decreased until eventually a structure of primary phosphate and eutectic was obtained. Micros 8 and 9 show top layer structures of slags 1 and 4, while micro 7 shows no primary ferrous

5

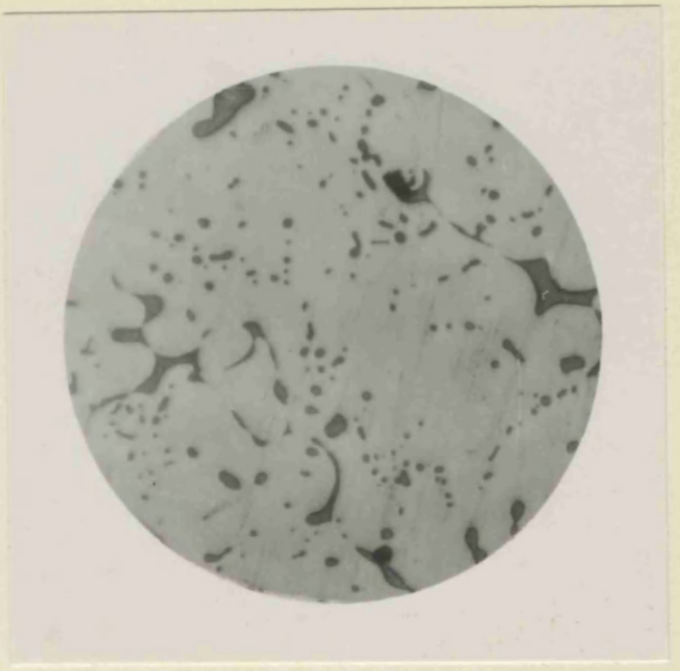
BOTTOM LAYER

SLAG 1.

80%FeO, 15%P_2O_5, 5% CaO.

TOP LAYER

6

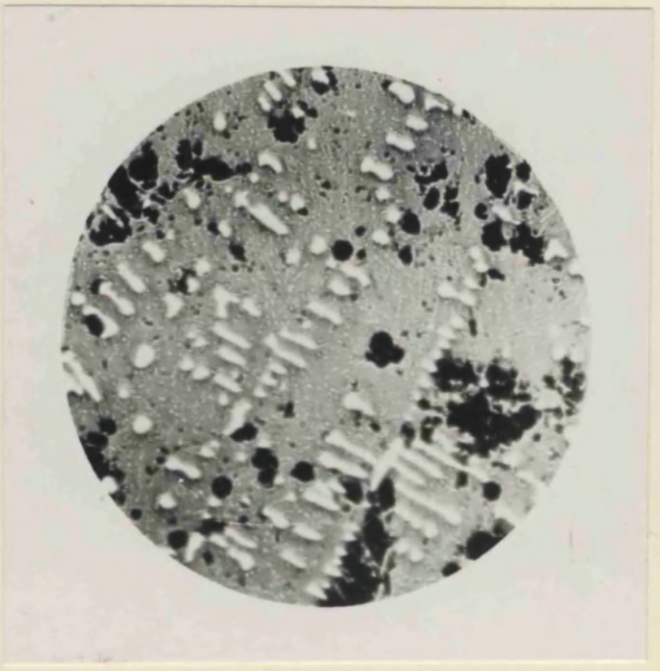


BOTTOM LAYER

SLAG 4.

70%FeO, 16%P_2O_5, 14%CaO.

TOP LAYER



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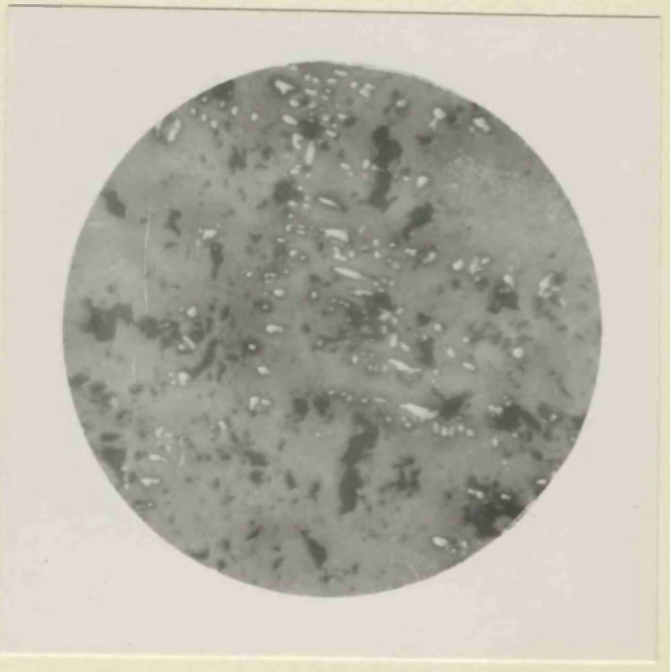
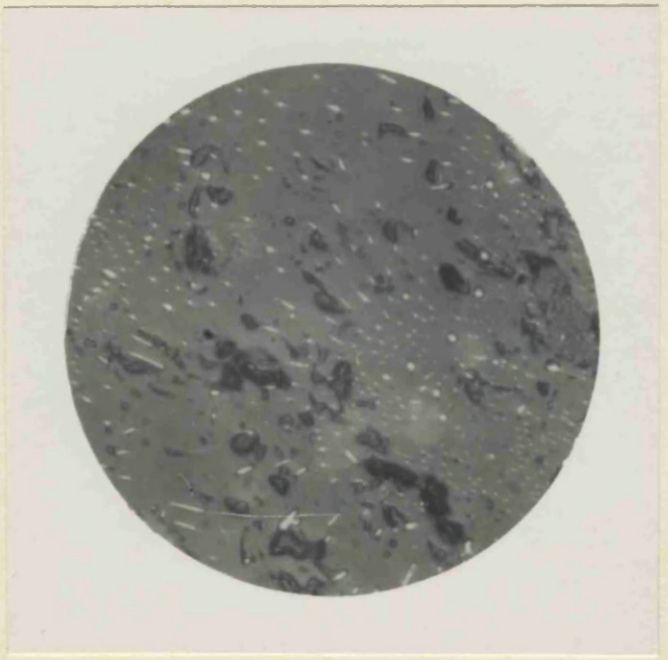


9

X100

UNETCHED

7



SLAG 8.

TOP LAYER

6·5% FeO, 1% Fe_2O_3, 5·6% MgO, 42·3% P_2O_5, 44% CaO.

X 500 UNETCHED

oxide crystals, and therefore would be expected to lie outwith the primary field of crystallisation of ferrous oxide. (The large dark areas in micro 7, can be attributed to the porous nature of the slag.)

On comparing the structures of the top and bottom layers of slag 1 (micros 5 and 8), it can be seen that a third light grey phase is associated with the ferrous oxide dendrites in the bottom layer only. There is little doubt that this is the same phase that was detected in the iron phosphate binary system, and as discussed then, may be attributed to Fe_3O_4. This suggestion is supported by the fact that the bottom layer slags contain more ferric oxide than top layer slags, so that more Fe_3O_4 would be expected to be present in the former.

C. Molybdenum Crucibles.

It was found that top layer compositions containing more than 40 per cent lime, could not be melted in iron crucibles. An attempt was therefore made to use molybdenum crucibles, to investigate these high melting point slags.

These crucibles, however, were attacked by the slags in the same way as was experienced when iron phosphate binary slags were superheated in iron crucibles. Attack again took place up the crucible walls, being more pronounced at the liquid surface and, as before, an unknown gas was evolved. As would be expected, the slag lost phosphorus and an alloy of iron, phosphorus and molybdenum was deposited at the base of the crucible. All slags were found to be contaminated with molybdenum (presumably as an oxide) and on one occasion the amount present was as great as 31.6 per cent MoO_3. Hence it was apparent that molybdenum was

unsuitable for this work and all subsequent high melting point slags were melted in slip-cast magnesia crucibles.

D. Magnesia Crucibles.

The performance of these crucibles was found to vary with the lower layer slag composition. With those compositions containing less than 12 per cent lime, the crucibles showed little slag penetration, but when lime was present in greater amounts, their resistance to slag attack depreciated very rapidly. Thus it was possible, only with great difficulty to retain the lower layers of slags 10 and 11.

There are two possible causes of crucible failure:-

(a) On a few occasions most of the top layer remained suspended across the crucible. This suggested that failure occurred after solidification of the top layer. On further cooling, spalling, caused by contraction of the crucible walls on the solid top layer, may have allowed the still liquid bottom layer to escape.

(b) The presence of calcium ferrites would be expected in those slags which showed excessive crucible attack. According to the phase diagram reported by White, Graham and Hay(23) and shown in Figure 12, a bottom layer composition containing such ferrites would have a comparatively low melting point, and should be extremely fluid at temperatures over 1500°C. Such a fluid slag would be expected to be highly corrosive to crucible materials, and it is believed that this is the more probable cause of crucible failure.

A feature of the slags melted in magnesia crucibles was that the line of demarcation between each layer was not so pronounced as with

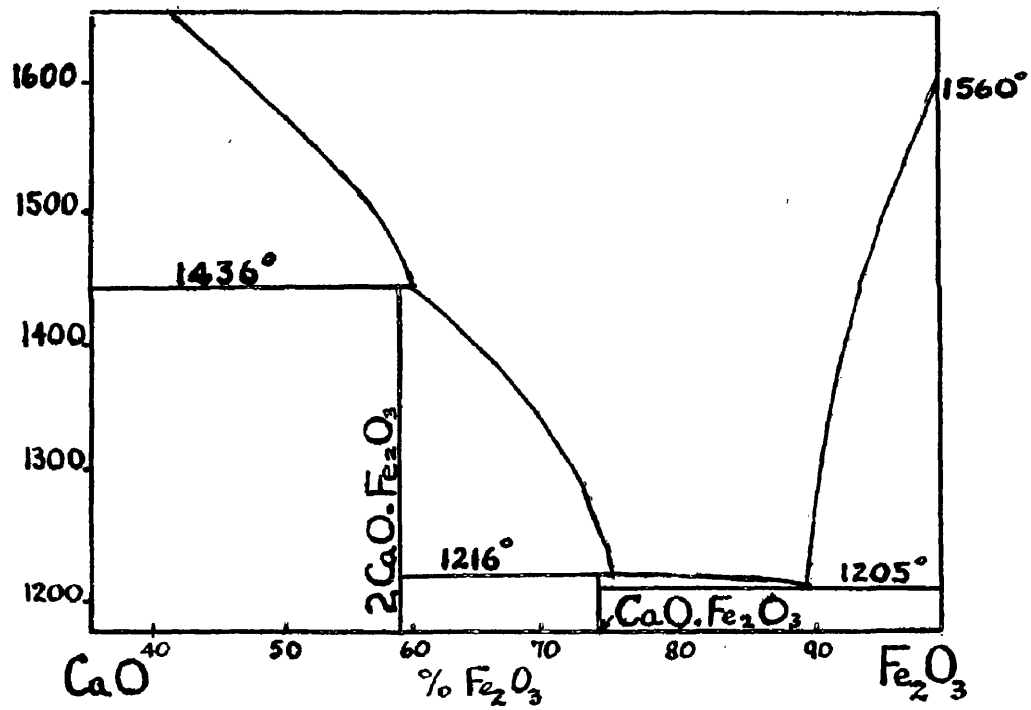

1600
1500
1400
1300
1200
1560°
1436°
1216°
1205°
2CaO.Fe2O3
CaO.Fe2O3
40
50
60
70
80
90
CaO
% Fe2O3
Fe2O3

FIG. 12.

slags melted in iron crucibles. This was especially the case when the layer compositions were close to one another (for example, slag 11), so that the sampling of each layer for chemical analysis became very difficult.

Figure 13, is a view of the layer interface of slag 8, in which the top half shows part of the underside of the top layer, and the bottom half, the upper surface of the lower layer. (This photograph also demonstrates the resistance to slag attack at 1540°C, shown by the magnesia crucibles employed in the investigation).

Microscopic examination of slags 10 and 11, yielded no information on account of the porous nature of the slags.

E. Immiscibility Loop Boundary at 1550°C.

Because of subsequent slag-metal experiments, carried out at 1550°C, it was of interest to investigate the boundary of the immiscibility loop at that temperature. A number of slag compositions within the loop were therefore heated to 1550°C., in slip-cast magnesia crucibles in an atmosphere of pure nitrogen, and rapidly cooled from that temperature. The results of chemical analysis of each layer are shown in Table 3, and plotted in Figure 14.

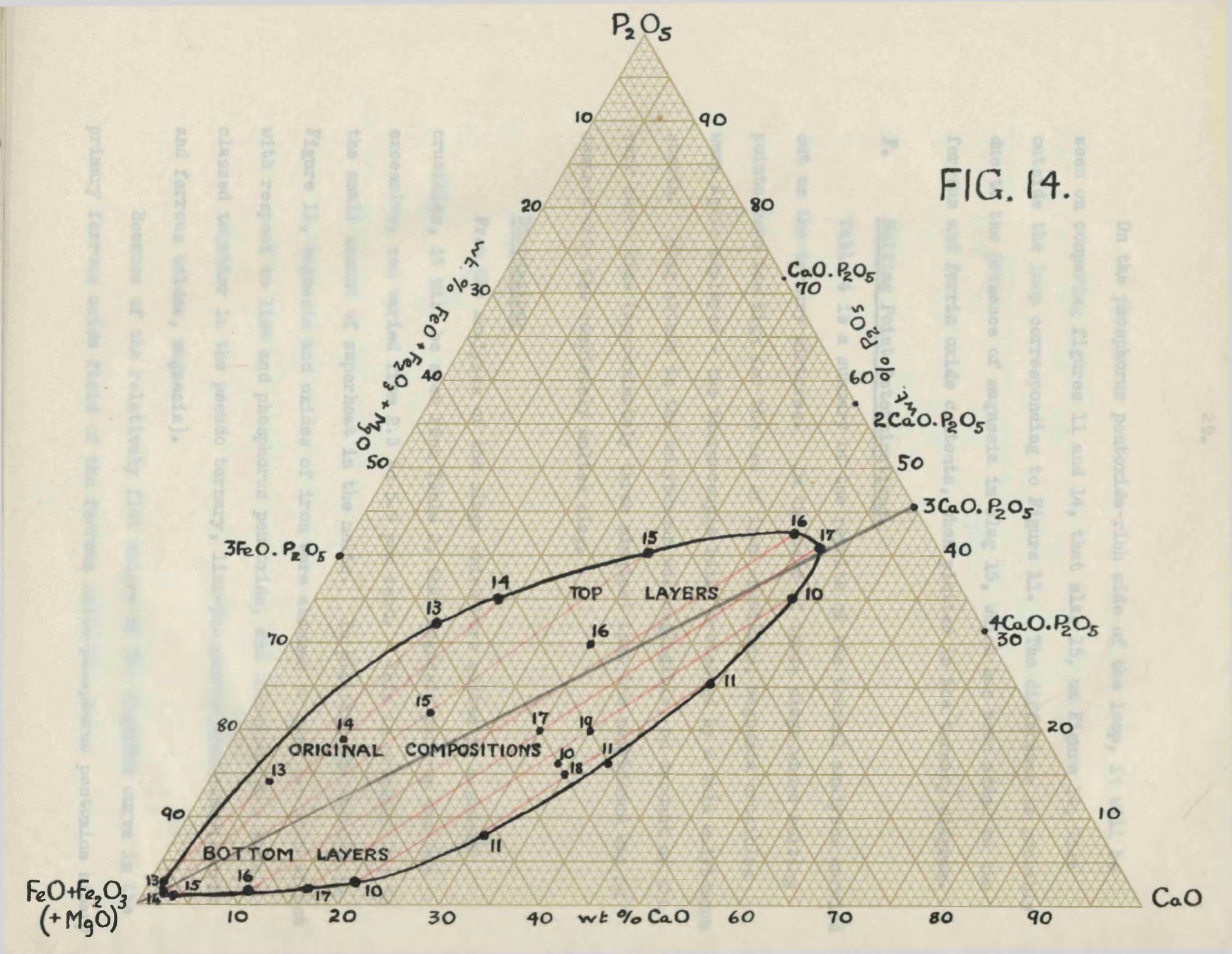
As was to be expected, slags 18 and 19 could not be retained by the magnesia crucibles at 1550°C and instead, the layer compositions corresponding to slags 10 and 11 were included in Table 3, and plotted in Figure 14. Since these slags were rapidly cooled from 1540 and 1520°C respectively, it was considered that their layer compositions would approximate those at 1550°C.

FIG. 13.

TABLE 3.

WEIGHT PER CENT.

Slag No.	Original Composition			Top Layer.				Bottom Layer.			
	FeO	CaO	P_2O_5	FeO	P_2O_5	CaO	MgO	FeO	P_2O_5	CaO	MgO
13	80	6	14	40.0	32.5	13.4	15.5	91.4	2.5	1.8	5.2
14	70	11	19	34.0	35.0	18.2	12.5	91.1	1.0	2.2	6.2
15	70	18	22	17.6	40.5	30.5	13.0	89.0	1.0	3.0	7.0
16	45	30	25	7.6	42.3	44.1	5.7	81.8	1.8	10.3	6.0
17	50	30	20	8.0	41.0	47.5	3.0	75.3	1.6	16.3	5.1
18	50	35	15	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
19	45	35	20	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
10	50	34	16	13.7	35.2	47.5	3.1	71.0	2.8	20.5	4.1
11	45	39	16	26.5	25.3	44.5	2.3	56.6	8.0	30.6	4.7


P2O5
FIG. 14.
CaO.P2O5
2CaO.P2O5
3CaO.P2O5
4CaO.P2O5
3FeO.P2O5
wt % P2O5
wt % FeO + Fe2O3 + MgO
wt % CaO
FeO+Fe2O3 (+MgO)
CaO
TOP LAYERS
ORIGINAL COMPOSITIONS
BOTTOM LAYERS

On the phosphorus pentoxide-rich side of the loop, it will be seen on comparing figures 11 and 14, that slag 15, on Figure 14, lies outside the loop corresponding to Figure 11. The difference is probably due to the presence of magnesia in slag 15, which has been added to the ferrous and ferric oxide contents, when plotted in the "ternary" diagram.

F. Melting Point Determinations.

Table 4 is a summary of the results of the thermal analyses carried out on the ternary mixtures. In the case of those slags whose melting points were too high for the use of iron crucibles, magnesia crucibles were again employed - the thermocouple being protected by a thin molybdenum sheath. Slag attack on the molybdenum was negligible, on account of the very short time (approximately three minutes) that the molybdenum was in contact with the completely molten slag.

Discussion.

From the analyses of the slags which were melted in magnesia crucibles, it will be seen from Table 2, that magnesia pick-up was not excessive, and varied from 2.3 to 5.9 per cent. This is probably due to the small amount of superheat in the melts. In plotting the results in Figure 11, magnesia and oxides of iron were assumed to have the same effect with respect to lime and phosphorus pentoxide, and therefore have been classed together in the pseudo ternary, lime-phosphorus pentoxide-(ferric and ferrous oxides, magnesia).

Because of the relatively flat nature of the liquidus curve in the primary ferrous oxide field of the ferrous oxide-phosphorus pentoxide binary

TABLE 4.

Slag No.	Composition (Wt.%). FeO	CaO	MgO	P_2O_5	Beginning of Melting.	End of Melting.	Crucible used.
T1	69.5	3.8		26.4	880 ‡	1050	Iron
T2	45.5	5.0		20.0	1115	1120	"
T3	59.5	10.2		30.1	1115	1130	"
T4	40.8	23.0		35.8	1310	1360	"
T5	21.5	38.0		39.9	1320	1368	"
T6	26.1	33.0		39.9	1310	1360	"
T7	30.0	30.4		39.2	1330	1360	"
T8	14.1	41.2	3.0	41.9	*	1490	Magnesia
T9	11.0	43.6	3.1	42.0	*	1520	"
T10	16.5	47.5	3.4	36.0	*	1535	"
T11	24.6	46.0	2.8	27.0	*	1520	"
T12	77.5	20.0		2.1	1310	1440	Iron
T13	89.0	10.0		1.0	1205	1250	"
T14	96.0	1.0		2.6	1125	1360	"

‡ Result probably low, due to supercooling.

* Could not be determined accurately.

diagram (Fig.10), a tendency to phase decomposition must exist in the liquid state. In such a case it appears that in the liquid, iron ions attempt to fulfil their full coordination with eight oxygen ions, while phosphorus ions simultaneously strive to form $PO_4^{\equiv}$ tetrahedra by surrounding themselves with four oxygen ions. Due to their small size, iron ions would find difficulty in fully co-ordinating themselves with such large groups as $PO_4^{\equiv}$ tetrahedra, and would therefore prefer to be associated only with free oxygen ions. With the introduction of lime extra oxygen ions become available. The iron ions can now surround themselves with the required oxygen ions (because of their greater bond strength $[\frac{\text{valency}}{\text{cation radius}}]$ than calcium ions) while the large calcium ions would find little difficulty in co-ordinating themselves with the large $PO_4^{\equiv}$ ions. Segregation is so great that two separate layers result - one containing virtually all the calcium and phosphate ions, the other composed mainly of iron and oxygen ions.

This theory finds support in Oelsen and Weimer's(24) observations, that separate additions of lithium oxide (Li_2O), sodium oxide (Na_2O), and barium oxide (BaO), to ferrous oxide-phosphorus pentoxide mixtures, also formed similar immiscibility gaps. In all these cases the bond strength of the added metal ion is less than that of iron, and since the magnesium ion bond strength is greater than that of iron, it is to be expected that magnesium would behave similarly to iron, in the lime-ferrous oxide-phosphorus pentoxide ternary system.

The positions of the tie-lines through slags 7 and 8 show the join, ferrous oxide-tricalcium phosphate to deviate from a quasi-binary section. From the melts made in iron crucibles, (slags 1 to 6), however, there is every indication that the ferrous oxide-tricalcium phosphate section suggested by Oelsen and Maetz(15), and shown in Fig.15, is correct. It should be noted, however, that melts made in iron crucibles are not comparable with those melted in magnesia as the latter are contaminated with crucible material. Moreover, it is incorrect to treat a system of four or five components, as one containing only three, so that it would be more appropriate to describe the relevant slags as belonging to the pseudo-quaternary, lime-(magnesia + ferrous oxide)-ferric oxide-phosphorus pentoxide.

When the slag compositions are plotted in such a quaternary system, it will be seen from Fig.16, that they fall on a surface which slopes away from the ferrous oxide (magnesia)-lime-phosphorus pentoxide ternary plane in such a manner that the top layer compositions lie nearer this ternary plane than the lower layer compositions. As the projection on the ferrous oxide (magnesia)-lime-ferric oxide plane shows (Fig.17), the distance of the lower layer compositions from the ferrous oxide (magnesia)-lime-phosphorus pentoxide plane also increases with lime content up to the nodal point on the lime side of the immiscibility gap. A certain proportion of ferric oxide is present in "pure" ferrous oxide slags. The percentage of ferric oxide increases with lime content, due to the formation of stable ferrites, and decreases with acid (phosphorus pentoxide) content of the slag due to the tendency of phosphorus pentoxide

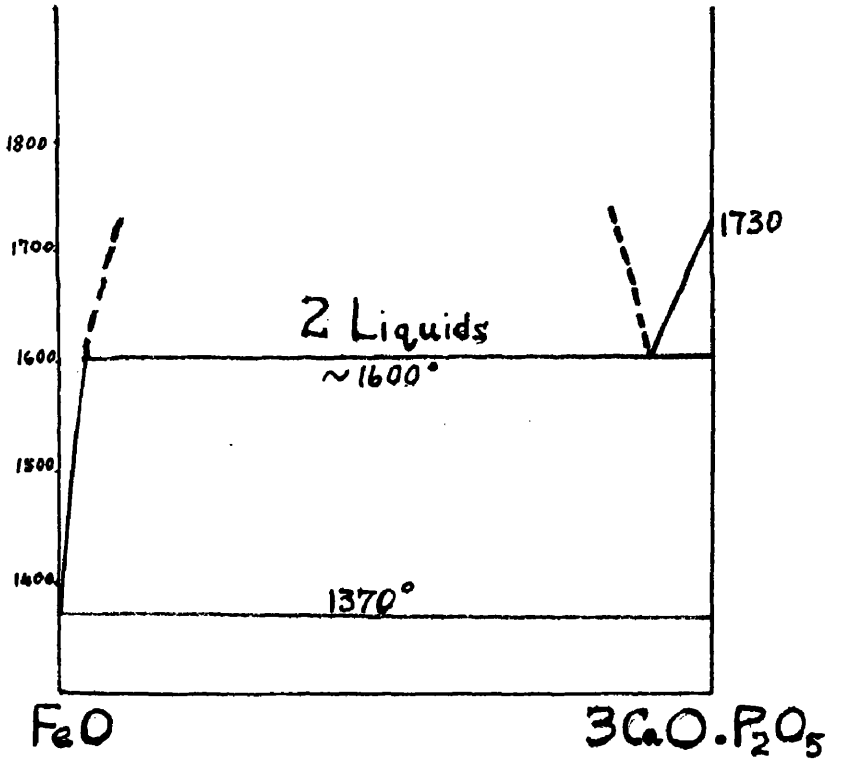

1800
1700
1600
1500
1400
1730
2 Liquids
~1600°
1370°
FeO
3CaO.P2O5

FIG. 15.

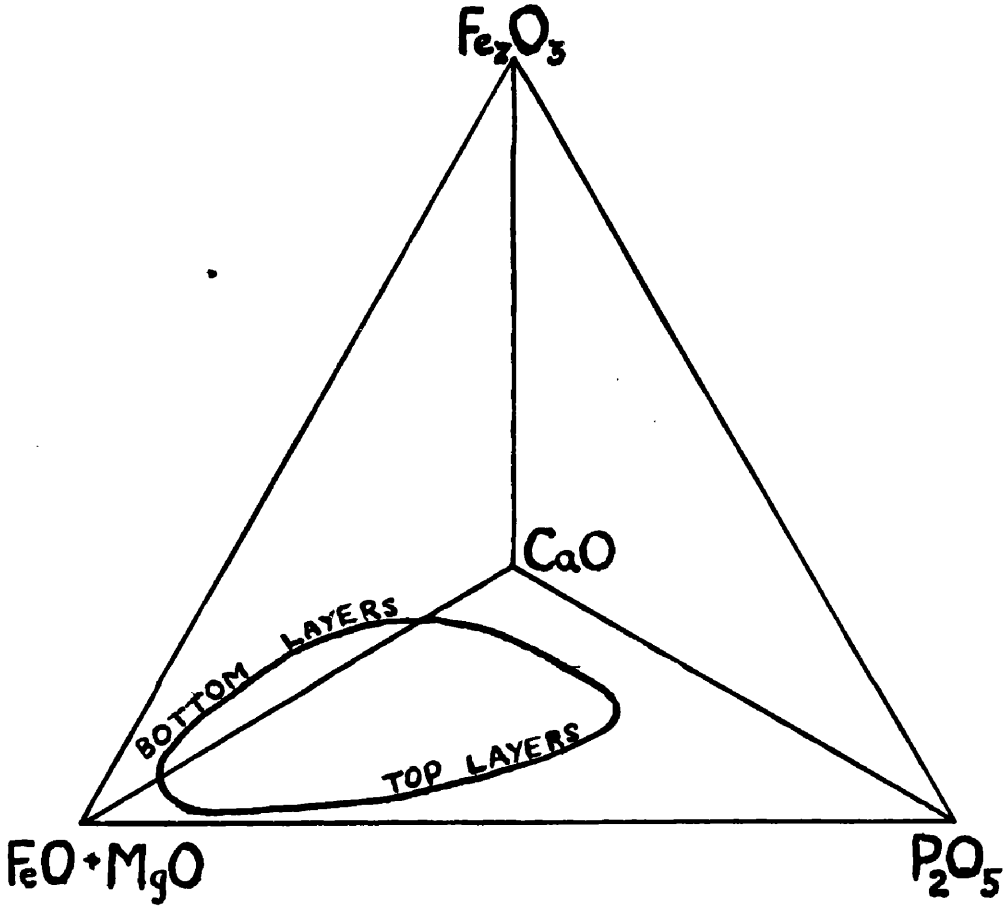


FIG. 16.

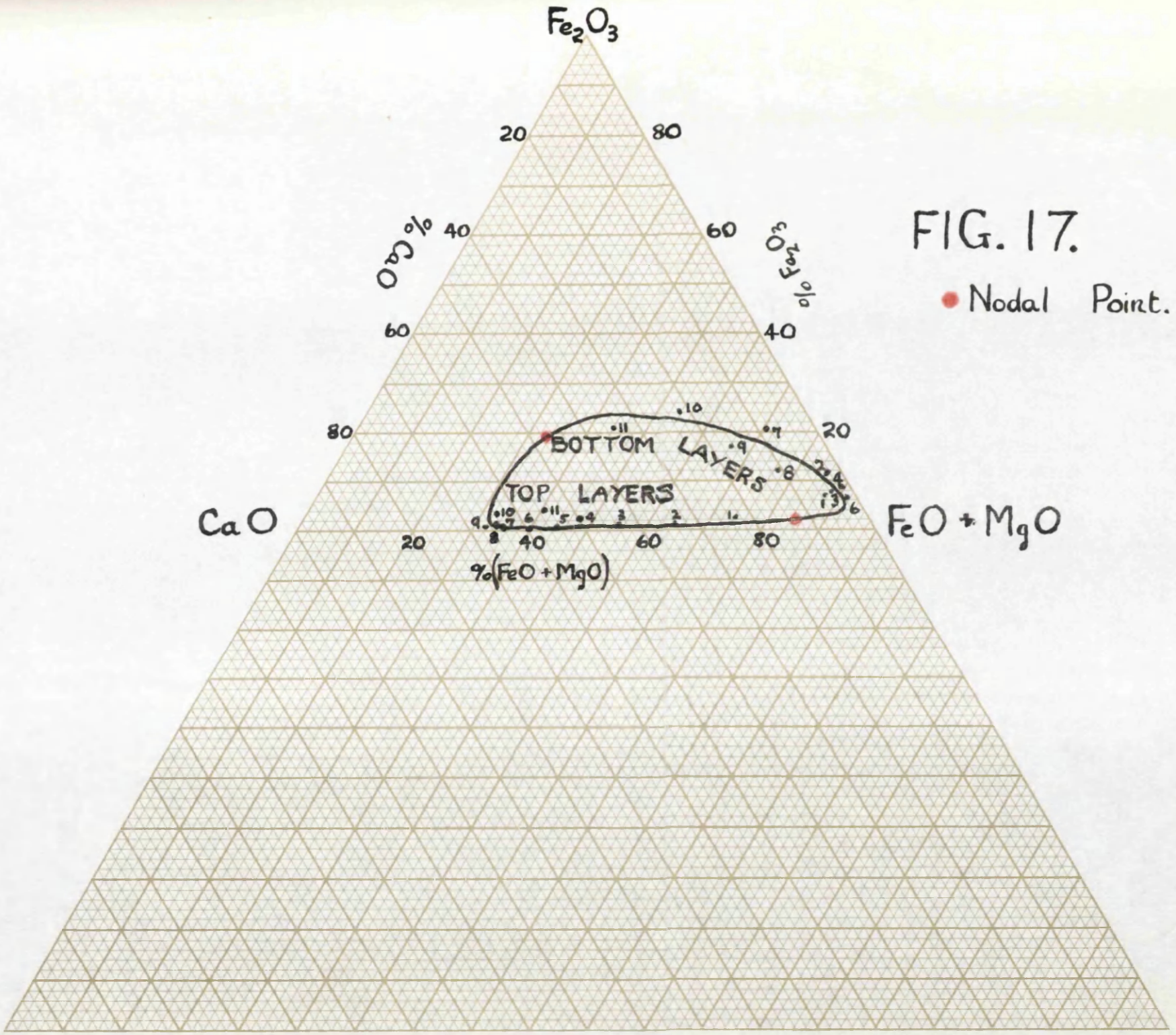


FIG. 17.

● Nodal Point.

to counter the stabilising effect of lime on ferrite formation, and also to the less important tendency to form ferrous orthophosphate. Hence the bottom layer compositions lie towards the ferric oxide corner of the quaternary system, and the axis of the elliptical immiscibility gap obtained in the present experiments does not lie in the ferrous oxide-lime-phosphorus pentoxide ternary plane.

Although the stabilising influence of magnesia, on phosphorus pentoxide is low, in comparison with lime, it exerts a slightly greater effect than ferrous oxide, so that, a small proportion of magnesia should be treated as equivalent to lime, and not as ferrous oxide. This would tend to shift the top layer compositions 7, 8, 9 in Fig.11, towards the lime corner of the diagram and also nearer to the ferrous oxide-tricalcium phosphate join. A similar adjustment in the plot would be unnecessary in the case of the lower layer compositions as the phosphorus pentoxide concentrations in these slags are exceedingly small, and magnesia would therefore be expected to be present, either in the form of ferrites or in solution with ferrous oxide.

Thus the deviation shown by the tie lines may be explained by the presence of ferric oxide in the lower layers, and a certain degree of equivalence shown by magnesia and lime in the top layers.

Moreover, if the join, ferrous-oxide-tricalcium phosphate were not a true binary section, the impossible situation would arise in which bottom layer slags on the lime-rich side of the binary join would be in equilibrium with other bottom layers on the phosphorus pentoxide side of the join. This is diagramatically represented in Fig.8. In iron

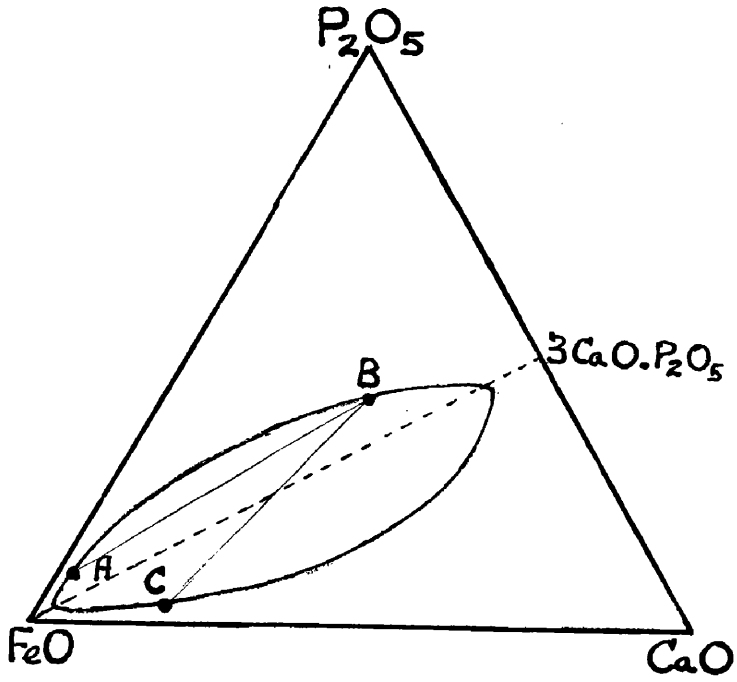


FIG. 18.

crucibles slag A is in equilibrium with top layer slag B, which when melted in a magnesia crucible would be in equilibrium with slag C. The effect of magnesia on the position of the tie-lines can also be seen on comparing the conode directions shown by similar slag compositions melted in both iron and magnesia containers. For example, slags 4 and 2 of Fig.11, should be compared with slags 15 and 14 in Fig.14.

A slight deviation from the expected join in the somewhat hypothetical system, lime-ferrous oxide-phosphorus pentoxide, has been reported, however, as a result of a slag-metal experiment carried out at 1600°C. by Trömel and Oelsen(25) in a tricalcium phosphate crucible. The layer compositions are reported in fig.11 as slag 12. The position of the lower layer composition of slag 12, and also of slag 6, in Fig.11, can be attributed to the effect of ferric oxide in the melts.

It should not be assumed, however, that the higher ferric oxide contents of slags 7 to 11, as compared with slags 1 to 6, can be attributed to the fact that the former slags were melted in magnesia crucibles. While it may be true that some ferric oxide is stabilised by magnesia, the difference is more likely to be caused by the following two factors:-

(a) the presence of greater quantities of lime in the melts made in magnesia crucibles.

(b) the reducing effect of iron on its higher oxides, in experiments carried out in iron crucibles.

Nevertheless, it is clear that large percentages of ferric oxide do not affect greatly the extent of immiscibility in the liquid state.

As was experienced in the $FeO-P_2O_5$ system, ternary slag compositions could not be superheated to any great extent in iron crucibles, without a change occurring in composition. Fig.19 shows the attack on a mild steel crucible, after slag 1 had been heated in it to 1450°C, for one hour. An indication of the presence of two immiscible layers can be seen clearly on examining the attack which took place. That attack proceeded to a similar extent in both layers, however, is to be expected as the activity of a given component, in top and bottom layers, would be the same.

The instability of ferrous orthophosphate in presence of iron, suggests that it is probably highly dissociated, which would result in a high activity of ferrous oxide and phosphorus pentoxide in the slag. Thus if the following mechanism for phosphorus removal in steelmaking is still valid, the activity of ferrous orthophosphate in the slag in equilibrium with molten iron is bound to be small;

$$2[P] + 5[O] \longrightarrow [P_2O_5]$$

$$[P_2O_5] + 3[FeO] \longrightarrow [3FeO.P_2O_5]$$

$$[3FeO.P_2O_5] \longrightarrow (3FeO.P_2O_5)$$

$$(3FeO.P_2O_5) + 3(CaO) \longrightarrow (3CaO.P_2O_5) + 3(FeO) \quad *$$

and for this reason the mechanism of phosphorus transfer from metal to slag, suggested by Carter(26) seems more probable; namely, that phosphorus pentoxide in the metal diffuses at the slag-metal interface into the slag where it forms tricalcium phosphate with the free lime present.

* Square brackets [ ] refer to metal concentrations, while
Round brackets ( ) refer to the slag phase.

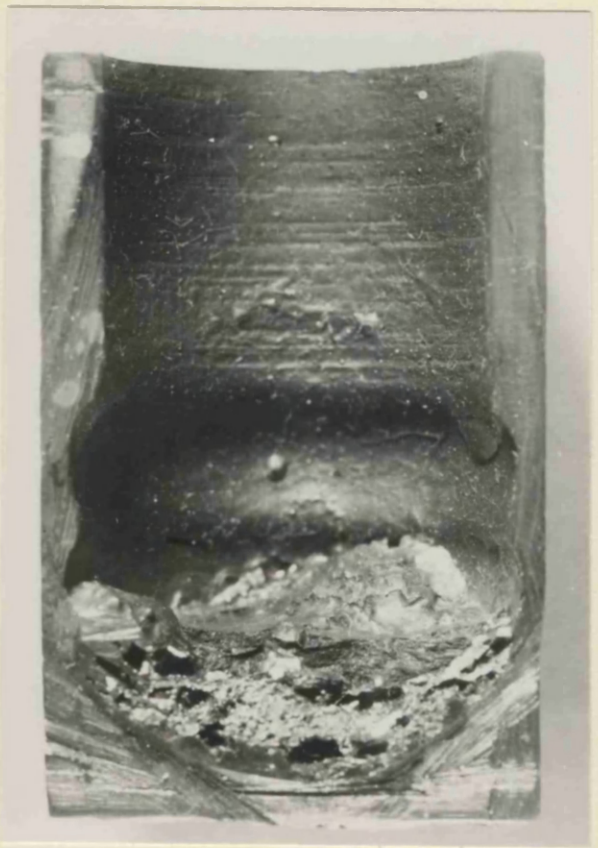


FIG. 19.

Discussion of Microscopic Examination.

Since in Fig.11, only slags 1-4, showed primary crystallisation of ferrous oxide, the corresponding top layer compositions must lie in the primary field of crystallisation of ferrous oxide, A binary crystallisation curve should therefore intersect the immiscibility loop, between the points corresponding to the top layer compositions of slags 4 and 5. Since such a curve could not cross the conodes within the two-layer region, it must follow the direction of the conodes until it reaches the opposite boundary of the gap, at a point between the lower layer slag compositions corresponding to slags 4 and 5. The curve of binary crystallisation would presumably continue in the homogeneous liquid region, outside the immiscibility loop until it reached the eutectic point in the ferrous oxide - tricalcium phosphate system. (It has been suggested by Oelsen and Maetz(15) that such a point exists). This implies that the temperature at which the binary crystallisation curve enters and leaves the immiscibility loop, must be lower than the eutectic temperature of the ferrous oxide-tricalcium phosphate binary system. The results of the melting point determinations (shown in Table 4) for the top layer compositions on the phosphorus pentoxide rich boundary of the immiscibility gap, show that the final freezing temperature falls gradually to the eutectic temperature in the ferrous oxide-phosphorus pentoxide binary system, (930°C). This suggests the existence of a complete series of solid solutions between ferrous and calcium orthophosphates, and also rejects the possibility of a ternary eutectic point in this region of the ternary system. The existence of a ternary

eutectic would imply the presence of three phases. In the microstructures examined, however, only two phases could be detected - ferrous oxide (light) and phosphate (dark), which would mean that either the orthophosphates are identical in colour and appearance, or that these compounds show appreciable solubility in the solid state. The first possibility seems unlikely, whereas the alternative is supported by the results of the melting point determinations. According to Oelsen and Maetz(15) twelve per cent of lime can be retained in solid solution by ferrous oxide. It is, therefore, not improbable that calcium and ferrous orthophosphates form a solid solution series, especially since di-calcium silicate ($2CaO.SiO_2$) and fayalite($2FeO.SiO_2$) have been shown(27) to have extensive solubility in the solid state.

Hence it would appear that the binary crystallisation curve which forms the upper boundary of the primary ferrous oxide liquidus surface emerges from the loop and then follows a path approximately parallel to the upper boundary of the immiscibility gap, as shown in Fig.11.

In this proposed representation of the diagram, slags 1 to 4 would be expected to show decreasing amounts of primary crystals of ferrous oxide, along with the binary eutectic of ferrous oxide and phosphate solid solution, while slags 5 to 8 would show primary crystals of phosphate solid solution, accompanied by the same eutectic. In all cases freezing would end at the binary eutectic curve shown.

The Liquidus Surface.

In the FeO-$3FeO.P_2O_5$-$3CaO.P_2O_5$ phase field, freezing ends at temperatures greater than 930°C, and as already described a binary eutectic trough would be expected to exist between a point on the immiscibility gap and the eutectic point in the ferrous oxide-phosphorus pentoxide binary system.

In the FeO-$3CaO.P_2O_5$-CaO field, initial freezing followed the monotectic crystallisation curve (T5-T11) shown in Fig.20, which shows the most probable section at 20 pct. P_2O_5. As the two layers crystallised separately, true equilibrium was not attained during freezing, and reliable solidus data were not obtained. Furthermore, as Fe_2O_3 increases with CaO content, the compositions are not even approximately ternary. It is probable, however, that a binary eutectic curve joins the FeO-$3CaO.P_2O_5$ eutectic point at ~1370°C (Oelsen and Maetz(15)) and a "ternary" eutectic point lying below the immiscibility loop. This curve must be close to the FeO-CaO system, because of the similar melting temperatures of bottom layer slags and those in the "FeO"-CaO system obtained by Hay and White(6).

Fig.20 shows that CaO additions to the nodal composition (T3 in Fig.20) produce a rise followed by a flattening of the ternary monotectic temperature. Further lime additions (beyond T5) produce a marked increase in this temperature, followed by a slight fall, so producing a ridge within the immiscibility loop. A sketch of the ternary monotectic surface is shown in Fig.21. The maximum temperature is 1540°C, which compares with a monotectic temperature of approximately 1600°C reported by Oelsen

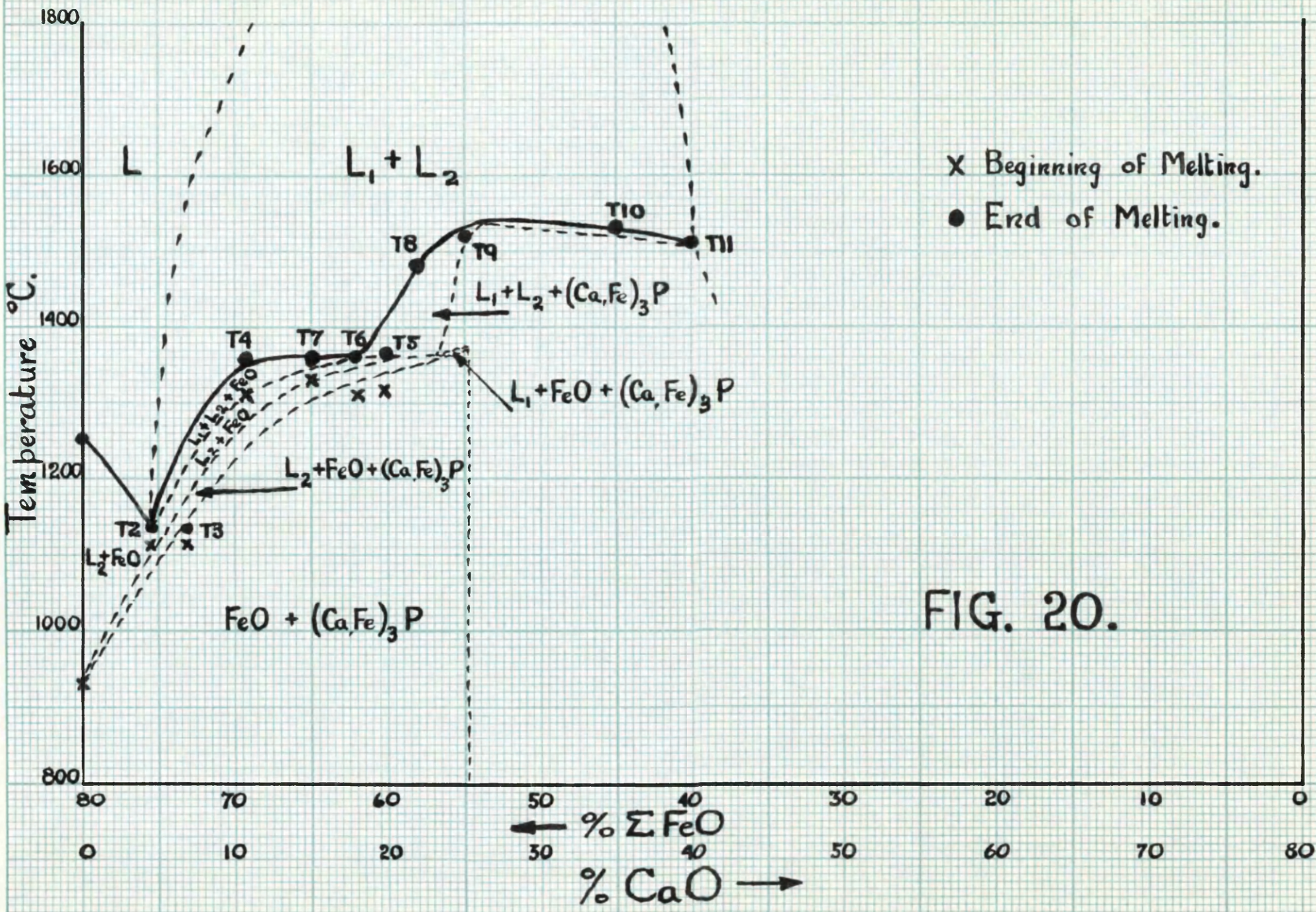
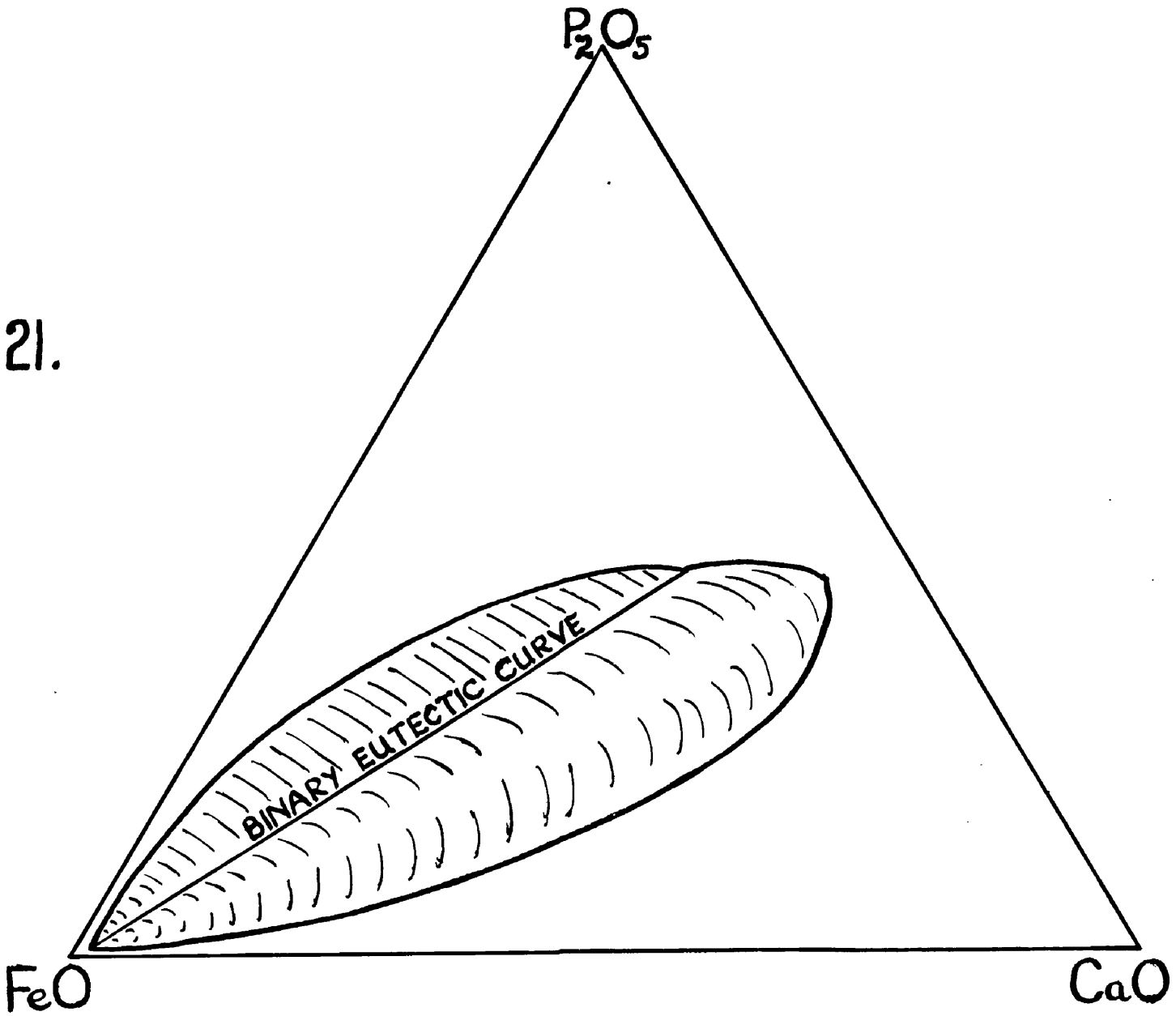

1800
1600
1400
1200
1000
800
Temperature °C.
L
L1 + L2
T10
T11
T8
T9
L1+L2+(Ca,Fe)3P
T4
T7
T6
T5
L1+FeO+(Ca,Fe)3P
L2+FeO+(Ca,Fe)3P
T2
T3
L2+FeO
FeO + (Ca,Fe)3P
80 70 60 50 40 30 20 10 0
0 10 20 30 40 50 60 70 80
← % ΣFeO
% CaO →
x Beginning of Melting.
● End of Melting.

FIG. 20.

FIG. 21.



and Maetz(15) for the ferrous oxide-tri-calcium phosphate join, and shown in Fig.15.

Analysis of the melts made in magnesia crucibles at 1550°C., implies that the boundaries of the immiscibility loop alter only slightly with temperature (cf. Figures 11 and 14) so that the loop would be expected to close only at very high temperatures.

An accurate prediction of the liquidus outside the immiscibility loop cannot be made, due to insufficient data. It is fairly certain, however, that there is a drop from the upper boundary of the loop to the binary trough, andalso to the liquidus surface in the eutectic region of the iron-phosphate binary system.

With regard to the lime-rich side of the immiscibility loop, the liquidus would be expected to fall to a binary eutectic trough, the location of which cannot be predicted, followed by a rapid rise to the lime corner of the ternary diagram, which would appear as a peak in the whole system.

The Ternary System, Ferrous Oxide-Lime-Phosphorus Pentoxide and its significance in Steelmaking.

The results in Fig.11 show that the region of immiscibility assumes a lenticular shape, stretching like a tongue from the ferrous oxide corner to a composition approaching that of tricalcium phosphate. It can be seen that the compositions of the top layers, which contain most of the lime and phosphorus pentoxide, lie on the smooth curve ABCD, whereas the bottom layers are essentially composed of ferrous oxide associated with small amounts of lime and phosphorus pentoxide,

and lie near the ferrous oxide corner of the ternary diagram. The results of the work carried out in iron crucibles are in substantial agreement with those of Oelsen and Maetz(15), while the boundary enclosing the lime-rich region also agrees with the prediction of these authors, and the experimental results of Trömel(10).

Due to the presence of the region of immiscibility the field of primary crystallisation of ferrous oxide has been extended. It can also be deduced that ferrous oxide melts are not miscible in all proportions with any of the phosphates of calcium, as the individual joins pass through the immiscibility loop.

Within the loop, the direction of the conodes indicates a critical composition A of low lime content, near the ferrous oxide-phosphorus pentoxide binary. That this composition is so near the binary, is further proof of the tendency of pure ferrous oxide-phosphorus pentoxide slags to separate into two layers. This is important with regard to work on the phosphorus reaction between iron and simple iron phosphate slags, as it explains why the application of the Law of Mass Action to these slags has proved so unsuccessful.

Another interesting fact, is that sufficient additions of ferrous oxide to any phosphate of calcium will eventually produce a ferrous oxide-rich phase. The phosphorus in the metal in equilibrium with these slags, will decrease steadily until phase decomposition in the liquid occurs, after which large overall increases in the ferrous oxide content of the slag will cause little change in both phosphorus and oxygen contents in the metal. This accounts for the phenomenen occasionally

encountered in the basic Bessemer process, in which an excessive increase in ferrous oxide in the slag (caused by overblowing) does not make any appreciable difference to the final oxygen and phosphorus concentrations in the steel.

PART II.

SLAG/METAL REACTIONS.

CHAPTER I.

The Phosphorus reaction in Steelmaking.

Factors such as temperature, degree of oxidation of the slag, basicity, etc., have long been known by steelmakers to have a great influence on the transfer of phosphorus from the metal to the slag. Any attempt to make a quantitative estimate of the relevant factors, however, has met with difficulties, principally because of the number of reactants concerned, and the complexity of the slags so produced.

A number of experimental investigations have been carried out, whose aim has been to explain more fully the phosphorus reaction in steelmaking. These have been summarised and reviewed recently by Carter(28). Early investigators(29-32) devoted their studies to the simple system consisting of iron containing phosphorus, and iron phosphate slags. The results of these investigations showed poor agreement as can be seen from the plot of phosphorus in the metal against phosphorus pentoxide in the slag, given in Figure 22. Thus, Maurer and Bischof(31) found a linear relationship to exist between phosphorus in the metal and phosphorus pentoxide in the slag, in ferrous oxide slags, up to 4 per cent phosphorus in the metal, whereas Schackmann and Krings(30 von Samson-Himmelstjerna(32) and Oelsen and Maetz(15) obtained roughly parallel curves showing a point of inflection.

At first sight, dephosphorisation would seem a direct oxidation of phosphorus by ferrous oxide, as follows:-

$$2[P] + 5(FeO) \longrightarrow (P_2O_5) + 5[Fe]$$

The fact that phosphorus pentoxide does not volatilize off in large quantities at steelmaking temperatures, would suggest that the reaction does not proceed far to the right unless the phosphorus pentoxide is

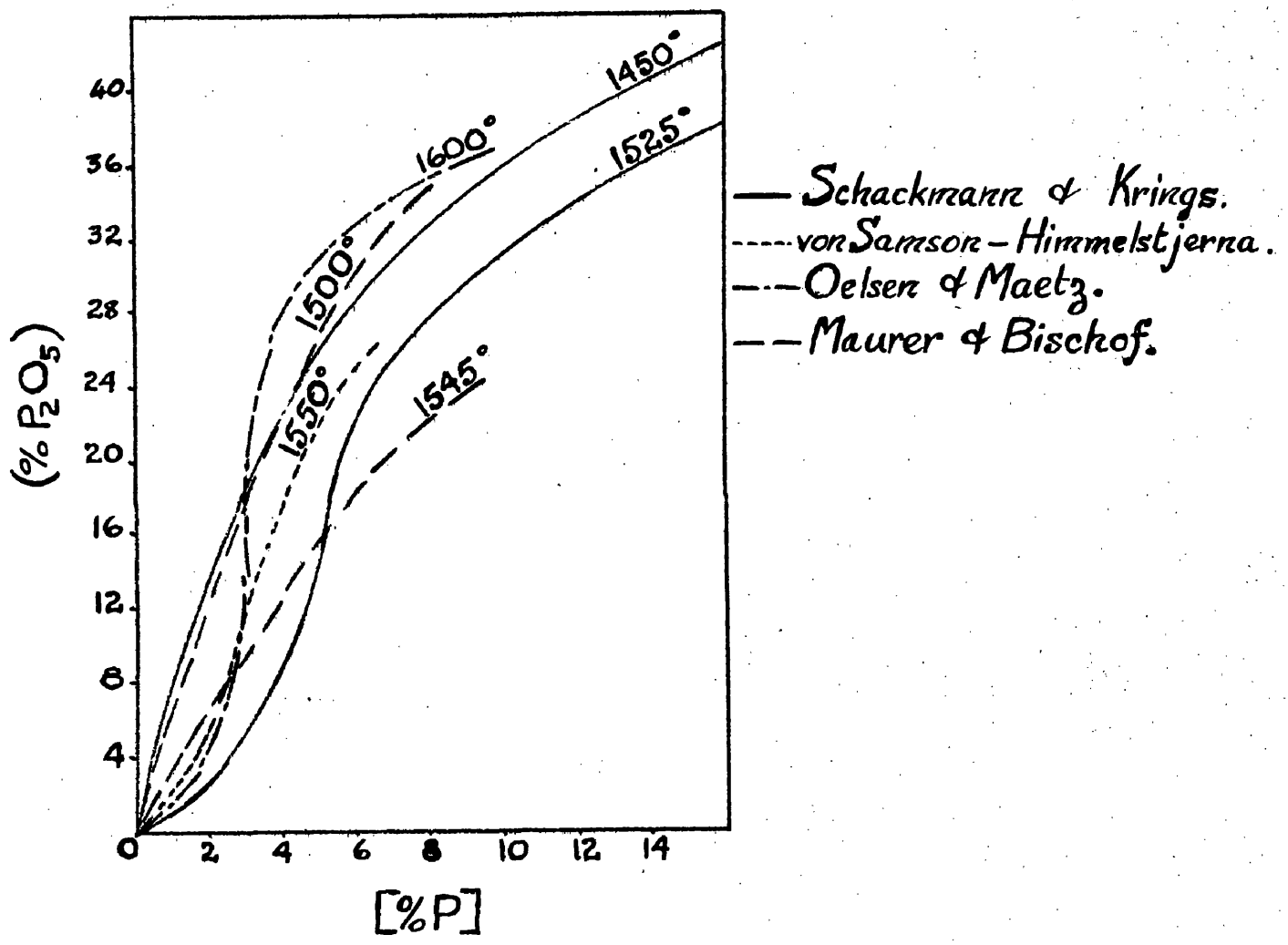

40
36
32
28
24
20
16
12
8
4
0
2
4
6
8
10
12
14
(% P_2O_5)
[%P]
1450°
1600°
1525°
1500°
1550°
1545°
— Schackmann & Krings.
----- von Samson-Himmelstjerna.
-·- Oelsen & Maetz.
– – Maurer & Bischof.

FIG. 22.

stabilised by phosphate formation. Similarly it is difficult to visualise the presence of elemental phosphorus in the metal, but it would seem more likely to exist as a phosphide of iron - probably Fe_3P. Schackmann and Krings based their reaction constant on the above equation but substituted the term [P] for $[P]^2$, on the grounds of incomplete knowledge of the state of combination of phosphorus in the metal. On the other hand, Maurer and Bischof found it impossible to formulate an equilibrium constant from their experimental results. Oelsen and Maetz, however, attributed the large variations in the slag-metal experimental data to a tendency to phase decomposition in liquid iron phosphate slags. According to them, separation was already brought about by the small amounts of impurities such as lime and alkali oxides which were present in the slag mixtures. Oelsen and Maetz(15) attributed the steeper course of their curve (Fig.22), compared with that of Schackmann and Krings(30), to the presence of magnesia dissolved from the crucible. It was assumed that magnesia increased the tendency to immiscibility more than did the alumina or zirconia, picked up from the crucibles used by Schackmann and Krings. These authors(30) also investigated the influence on the phosphorus reaction, of other oxides, such as silica, magnesia and lime, which were known to be present in steelmaking slags, and it was established that lime, and to a lesser extent magnesia, favoured dephosphorisation while alumina seemed to have no effect and silica greatly impaired phosphorus removal.

Most of the work using complex slags has, however, been carried out with the aid of steelworks data, and attempts have been made to correlate the phosphorus distribution with slag composition, temperature and other relevant variables.

In their intensive study of basic Bessemer and open hearth heats, Schenck and Riess(33) assumed that each slag constituent was present both in the free state, and in combination. They then calculated the "free concentration" for each constituent, but were still unable to formulate quantitatively the phosphorus equilibrium constant, without employing an empirical correction factor which depended on the phosphorus pentoxide content of the slag. Thus Schenck and Riess represented phosphorus removal by the following equations:-

$$2[P] + 5(FeO) + 3(CaO) \longrightarrow (3CaO.P_2O_5) + 5[Fe]$$

for which $\log K_p^{\overline{III}} = -\log \frac{(\Sigma P_2O_5)}{[\%P](FeO)^5(CaO)^3} + 0.045(\Sigma P_2O_5)$

and assuming the formation of tetracalcium phosphate,

$$2[P] + 5(FeO) + 4(CaO) \longrightarrow (4CaO.P_2O_5) + 5[Fe]$$

which gave $\log K_p^{\overline{IV}} = -\log \frac{(\Sigma P_2O_5)}{[\%P](FeO)^5(CaO)^4} + 0.060(\Sigma P_2O_5)$

As in the evaluations of Maurer and Bischof(31) and Schackmann and Krings (30), instead of $[P]^2$ only the first power was used. To explain this Schenck and Riess(33) suggested that phosphorus dissolved in molten iron might be present as double molecules of iron phosphide - namely $(Fe_3P)_2$. They attributed the necessity for the correction factors, in both equations, to the non-ideal behaviour shown by phosphate slags.

It is worthy of note that Zea(34) in a survey of the methods available for calculating the phosphorus content in the metal, for a given bath condition, found that of Schenck and Riess gave the best agreement with works practice.

In the laboratory, Balajiva, Quarrell and Vajragupta(35), made a comprehensive study of the phosphorus reaction using complex slags more closely related to those obtained in steelmaking. Experiments were carried out at 1585°C. in a small electric arc furnace, and they assumed the reaction occurring to be:-

$$2[P] + 5(FeO) + 3(CaO) \longrightarrow (3CaO.P_2O_5) + 5[Fe]$$

In formulating a constant for this equation they treated the slag components as behaving ideally,

$$\text{whence} \qquad K = \frac{(\%P_2O_5)}{[\%P]^2(\%FeO)^5(\%CaO)^3}$$

Their results showed the main factors in dephosphorisation to be, the concentration of ferrous oxide, (expressed either as "total iron" or as chemically analysed ferrous oxide), lime and phosphorus pentoxide in the slag. Manganous oxide and magnesia appeared to have no effect on the slag-metal equilibrium, other than acting as diluents.

In estimating the "free lime" present, the compounds dicalcium silicate ($2CaO.SiO_2$) and tricalcium phosphate ($3CaO.P_2O_5$) were assumed to be present in the liquid state, as they had been detected in quenched slag samples. It was shown by statistical methods that the lime combined as ferrite was most satisfactorily represented by $0.75\ CaO.Fe_2O_3$.

Thus $(CaO) = (\Sigma CaO) - (CaO)_{2CaO.SiO_2} - (CaO)_{3CaO.P_2O_5} - (CaO)_{0.75CaO.Fe_2O_3}$

Their results showed that log(CaO), so calculated, varied linearly with log k, where $k = \frac{(P_2O_5)}{[P]^2(FeO)^5}$.

The effect of temperature on the phosphorus reaction was later studied by Balajiva and Vajragupta(36) in a series of experiments carried out at 1550 and 1635°C. Results from this investigation were in agreement with those obtained at 1585°C and it was found that the relation between log k and log(CaO) at these temperatures could be expressed more generally by the equation

$$\log k = n \log(CaO) - c$$

where n was a constant, and c varied with temperature.

A similar investigation to that of Quarrell(35) and co-workers, using relatively complex slags, was carried out by Winkler and Chipman(37) but in this case the melts were made in magnesia crucibles, using inducation heating, and a thin layer of slag.

The predominating phosphate formed in the slag was assumed to be calcium tetraphosphate ($4CaO.P_2O_5$) and the equation for its formation was assumed to be

$$2[Fe_3P] + 5(FeO) + 4(CaO) \longrightarrow (4CaO.P_2O_5) + 11[Fe]$$

for which the equilibrium constant was given by the relation

$$K_P = \frac{(4CaO.P_2O_5)}{[P]^2[O]^5(CaO)^4}$$

In evaluating Kp, the activity of ferrous oxide in the slag was related to the oxygen content of the metal, and the term (CaO^1) referred to the free or uncombined lime in the slag. As was experienced by Quarrell(35) and co-workers, certain assumptions concerning the slag constitution had to be made before (CaO^1) could be calculated. In the ferrous oxide activity determinations of ferrous oxide-lime-magnesia-silica slags, Fetters and Chipman(38) had found that those slags could be regarded as behaving ideally, if dicalcium silicate were assumed to be present as double molecules - $(2CaO.SiO_2)_2$. A similar assumption was made by Winkler and Chipman(37) in estimating the activity of lime in their slags, but after accounting for the lime associated as tetra-calcium phosphate, calcium ferrite, and aluminate, it was necessary to further assume a certain degree of dissociation of the double molecules according to the equation

$$(2CaO.SiO_2)_2 \longrightarrow 2CaO.2SiO_2 + 2CaO.$$

Within the limits of slag composition studied, lime, magnesia and manganous oxide were found to be equally effective in dephosphorisation and their concentrations were therefore added; and together with the "lime" produced in the silicate dissociation, the term (CaO^1) was finally expressed as (Σ Base).

In the investigations of Schenck and Riess(33), Quarrell(35,36) and co-workers, and Winkler and Chipman(37) essentially the same method of evaluating activities or free concentrations has been used - namely, the presupposing of certain undissociated compounds in the liquid slag, and thereafter calculating the remainder as the free concentration of each component. Although this method gave fairly satisfactory results

when applied to steelmaking practice there is no doubt that Schenck and Riess were led to highly improbable conclusions concerning the constitution of basic open hearth tapping slags; for instance monocalcium silicate ($CaO.SiO_2$) was considered to be the main silicate present.

Unlike Schenck and Riess, the other investigators ~~both~~ assumed equations for the phosphorus reaction and endeavoured to bring their experimental results into line with them. Their methods of doing so, however, are open to criticism - the main one being the assumption that phosphate slags behave ideally. With regard to Winkler and Chipman's work, the concept that the main basic oxides encountered in steelmaking have equivalent dephosphorising powers, implies equal stability of the different phosphates. This implication is quite wrong, as it has been shown by Bookey(39) and Pearson and co-workers(20), that the orthophosphates of both magnesium and manganese are considerably less stable than calcium orthophosphate.

Recently, Fischer and vom Ende(40) studied the phosphorus reaction, using lime crucibles and simple slags containing ferrous oxide, lime and phosphorus pentoxide, at temperatures between 1530 and 1700°C. Since lime was one of the main slag components, contamination from the crucible was eliminated, but on the other hand, all the slags should be saturated with lime at the working temperature. Thus, all the equilibrium slag compositions lay on the lime-rich side of the immiscibility loop. Microscopic and X-ray examinations of the slags, however, showed tri-calcium phosphate to be present as the primary phase, on a background of eutectic. This is rather surprising as the majority

of the slag compositions lay in what would be expected to be the primary separation field of lime.

These authors also found little variation in the activity of ferrous oxide (calculated from the oxygen content of the metal) in slags containing between 20 and 50 per cent iron, and attributed this non-ideal behaviour, to the presence of the immiscibility loop in close proximity to the slag compositions studied. Phase decomposition in the liquid state, however, was never observed.

In formulating an equilibrium constant for the reaction

$$2[P] + 5[O] + 3(CaO) \longrightarrow (3CaO.P_2O_5)$$

for which $$K = \frac{(3CaO.P_2O_5)}{[P]^2[O]^5(CaO)^3}$$

it was found that log K was dependent on the phosphorus pentoxide content of the slag, when the terms [P] and [O] were expressed as weight percentages and $(3CaO.P_2O_5)$ and (CaO) in mole fractions. When the activities of tricalcium phosphate and lime were assumed equal to unity, the equation then took the form

$$K_1 = \frac{1}{[P]^2[O]^5}$$

This equation was considered to be applicable to the above reaction, as the plot of log [O] against log [P] approximated a straight line of slope - 0.4.

Theoretically it is only permissible to assume the activity of lime equal to unity, because of the presence of solid lime in the system, but the assumption concerning tricalcium phosphate was

probably supported by its presence as the primary phase in all the slag compositions. In the plot of log [O] against log [P], however, it is more probable that the small variation in K_1 can be attributed to a relatively constant rather than a unit phosphate activity. The observation concerning the constancy of the activity of ferrous oxide in the same slag range would support this.

The early conductivity experiments carried out on molten slags by Wejnarth(41), showed that liquid slags must possess a certain amount of ionic character, and Herasymenko(42) was the first to make a serious attempt to use the ionic theory as a means of explaining slag-metal equilibria. He assumed that all slag components were completely ionised such that, Fe^{++}, Fe^{+++}, Ca^{++}, Mg^{++}, Mn^{++} .....were regarded as cations, and $O^{=}$, $PO_4^{\equiv}$, $SiO_4^{\equiv}$ ....as anions. In his calculations all slag concentrations were expressed as ionic fractions, that is, the number of gram ions, of the ion considered, divided by the total number of positive and negative ions.

Removal of phosphorus from metal to slag was represented by the ionic equation,

$$[P] + \tfrac{5}{2}(Fe^{++}) + 4(O^{=}) = (PO_4^{\equiv}) + \tfrac{5}{2}[Fe]$$

such that -

$$K = \frac{(PO_4^{\equiv})}{[P](Fe^{++})^{\frac{5}{2}}(O^{=})^4}$$

"K" was found to vary with the concentrations of (Ca^{++}) and $(O^{=})$, and for this reason it was called an Equilibrium Ratio.

A similar variable "constant" was later found by Herasymenko and Speight(43) in a more detailed study of phosphorus removal. The equation used in this case was $[2P] + 5[O] + 3(O^{=}) \longrightarrow 2(PO_4^{\equiv})$

which gave rise to $K = \frac{(PO_4^{\equiv})}{[P][O]^{\frac{5}{2}}(O^{=})^{\frac{3}{2}}}$

Since the concentrations of each ion were expressed in ionic fractions, constancy of K, would have implied ideality - that is, the ions of the slag would be expected to be randomly mixed, irrespective of charge or sign. It would seem more likely, however, that positive ions are surrounded by negative ions and vice versa.

Even with this model, however, steelmaking slags cannot be regarded as perfect ionic solutions. In order to account for the preferential association of certain ions, the simpler theory of Herasymenko (42) has given way to the more elaborate modifications of Flood and Grjotheim(44). In their equations these authors have recognised, that in a liquid slag, phosphate ($PO_4^{\equiv}$) ions would not be associated with the cations present, in proportion to their ionic fractions, because of the differences in energies of interaction between the phosphate ions and the various cations. If the energies of interaction had been equal, this would have implied equal phosphate stability in the liquid state, and consequently an equivalent dephosphorising power of all the cations present.

In formulating an equilibrium constant, they assumed the equation of Herasymenko and Speight(43), which gave

$$K = \frac{(PO_4^{\equiv})^2}{[P]^2[O]^5(O^{=})^3}$$

The influence of cationic composition was introduced by using the expression

$$\log K = N_{M^{++}} \cdot \log K'_{M^{++}}$$

where M = Ca, Fe, Mn, Mg .....

$N_{M^{++}}$ was the ionic fraction of the various cations present, for example, $N_{Ca^{++}}$ was the ratio of the (Ca^{++}) ion charges to the total number of cation charges present,

and $K'_{M^{++}}$ corresponded to the equilibrium

$$2[P] + 5[O] + 3[MO] \longrightarrow (3MO.P_2O_5)$$

When expanded, $\log K = N_{Fe^{++}} \log K'_{Fe^{++}} + N_{Mg^{++}} \log K'_{Mg^{++}} + N_{Ca^{++}} \log K'_{Ca^{++}}$.....

where $K'_{Fe^{++}}$ referred to the equation $2[P] + 5[O] + 3(FeO) \longrightarrow (3FeO.P_2O_5)$

and $K'_{Mg^{++}}$ " " " $2[P] + 5[O] + 3(MgO) \longrightarrow (3MgO.P_2O_5)$

and $K'_{Ca^{++}}$ " " " $2[P] + 5[O] + 3(CaO) \longrightarrow (3CaO.P_2O_5)$

It will be seen that the assessing of log K required a knowledge of the equilibrium constant for each subsidiary reaction. Flood and Grjotheim were able to obtain values of 21 and 12 for $\log K'_{Ca^{++}}$ and $\log K'_{Fe^{++}}$, from Winkler and Chipman's results, but, because of insufficient data, values for $\log K'_{Mn^{++}}$ and $\log K'_{Mg^{++}}$ could not be obtained. Best agreement between observed and calculated values was obtained when 13 and 18 were substituted in the equation, such that

$$\log K' = 12N_{Fe^{++}} + 13N_{Mn^{++}} + 18N_{Mg^{++}} + 21N_{Ca^{++}}.$$

In a recent paper, Turkdogan and Pearson(45) calculated an equilibrium constant for the phosphorus reaction which could be applied to steelmaking slags, by making use of new and existing thermodynamic data (39,46-48). Thus in the equation

$$2[P] + 5[O] \longrightarrow (P_2O_5)liq.$$

it was shown that

$$\log K = \log \frac{(P_2O_5)liq.}{[P]^2[O]^5}$$

$$= \frac{36,850}{T} - 29.07$$

(under steelmaking conditions, oxygen and phosphorus dissolved in molten iron were assumed to obey Henry's Law).

This equation was found to be valid, when the oxygen concentration was calculated from the activity of ferrous oxide in the slag, using the relationship reported by Taylor and Chipman(49)

$$L_{FeO} = \frac{[O]}{(aFeO)}$$

and their ferrous oxide activity chart,(50), so that the above equation could be written

$$2[P] + 5(FeO) \longrightarrow (P_2O_5) + 5[Fe]$$

for which $\log K_p = \log \frac{(aP_2O_5)}{(aFeO)^5\ [P]^2}$

$$= \frac{5250}{T} - 15.4$$

Turkdogan and Pearson(45) found, however, that the activity coefficient of phosphorus pentoxide, varied considerably with slag composition, and to account for this, use was made of an equation, similar to that of Flood and Grjotheim, which incorporated oxides instead of ions.

Thus $\log \gamma_{P_2O_5} = -1.12 \Sigma AiNi + b$

where $\Sigma AiNi = 22N_{CaO} + 15N_{MgO} + 13N_{MnO} + 12N_{FeO} + 31N_F - 2N_{SiO_2}$

Ni was the mole fraction of each constituent, and b was a measure of the temperature dependence of the activity coefficient of phosphorus pentoxide; b varied with temperature according to the following relation

$$b = \frac{-42,000}{T} + 23.56$$

Turkdogan and Pearson determined values of Ai, by trial and error, to give best agreement with works data and the results of Fischer and Vom Ende(40), and Quarrell and co-workers(35).

Turkdogan and Pearson(51) claimed good agreement with steelmaking data, but failed to find any correlation with the results of Winkler and Chipman's investigation. This is interesting as their equation is very similar to that of Flood and Grjotheim(44), who based their equation on Winkler and Chipman's data, and as might be expected, good agreement existed between the calculated and observed experimental data. Good agreement was also obtained by Flood and Grjotheim(52), when a similar equation for the manganese equilibrium was applied to the ferrous oxide-manganese oxide-magnesia-silica slags used by Bell, Murad and Carter(53). Up to the present, however, there is no evidence of the equations of Flood and Grjotheim(44) being applied to actual basic open hearth steelmaking data, or to the results of other investigations.

Phosphorus removal in steelmaking should be treated as an interfacial reaction between metal and slag, under which conditions the metal oxygen concentration at the interface would be expected to vary appreciably from the oxygen content in the bulk of the metal. Hence, it is more probable that the ferrous oxide content of the slag would be of greater significance in dephosphorisation than the oxygen content of the metal. In applying Flood and Grjotheim's equation to steelmaking data it would therefore probably be necessary to use the metal oxygen content calculated from the slag composition, rather than the analysed oxygen content, because the oxygen potential corresponding to the latter is invariably less than that in the slag, due to carbon removal(54).

Activity Coefficients of Phosphorus and Oxygen in Molten Iron.

Pearson and Turkdogan(55) have investigated the effect of phosphorus on the activity coefficient of oxygen in molten iron at steelmaking temperatures. In their experiments, iron-phosphorus alloys were melted and brought to equilibrium with a controlled atmosphere of hydrogen and water. Under these conditions, the oxygen concentration in the metal depended on the temperature, the oxygen potential of the gas phase, and the phosphorus content of the metal. The oxygen activity in the metal was calculated from the gas-metal equilibrium data reported by Dastur and Chipman(48) and when compared with the analysed concentration, it was concluded that phosphorus reduced the activity coefficient of oxygen to the extent

$$\log f_o^P = -0.032\ [\%P]$$

Using a modified form of Wagner's(56) relationship, the influence of oxygen on the activity coefficient of phosphorus was then calculated to be

$$\log f_p^O = -0.062\ [\%O]$$

This work confirmed quantitatively some previous observations of Bookey, Richardson and Welch(57) who conducted similar investigations in lime, and calcium phosphate crucibles. At low oxygen activities, and therefore low oxygen and high phosphorus concentrations in the melt, these authors found log $p\frac{H_2O}{H_2}$ to be linearly related to log [%P]. At higher oxygen, and lower phosphorus concentrations, however, this relationship no longer existed and the deviation was attributed to the effect of oxygen on the activity of phosphorus. This effect decreased rapidly with increase in temperature. Thus at 1540°C, it appeared at phosphorus contents up to 0.8 per cent whereas at 1580°C, it only became evident below 0.03 per cent phosphorus.

CHAPTER 2:

Slag-Metal Experimental Work and Results.

A. Apparatus and Materials used.

1. Materials.

(a) The preparation of ferrous oxide, lime and calcium phosphate has been described in Part I, Chapter 2.

(b) Iron - "Armco" iron was used.

(c) Iron - Phosphorus Master Alloys. The preparation of iron-phosphorus alloys of approximately predetermined composition was simplified by the use of a master alloy, which contained about eight per cent phosphorus and was prepared by the addition of red phosphorus to molten "Armco" iron. The apparatus used was a simplified design of that used by Haughton(58) and is shown in Figure 23.

The apparatus was assembled and side arm A, was charged with pellets of red phosphorus (each about 1.3 grams. in weight) and the bung secured. Air was swept out of the system by introducing nitrogen through B. The induction heating was then switched on and when the iron had melted, the first pellet was added by pushing wire C along the side arm. The reaction between the iron and each pellet was viewed through the observation window, and when completed, more phosphorus was added. It was found that a maximum number of ten pellets could be added to one hundred grams of iron, as further additions led to large losses of phosphorus through the exit end D, and crucible failure due to slag attack.

Some phosphorus also condensed in the yellow form on the colder parts of the silica tube, so that particular care was necessary in dismantling the apparatus.

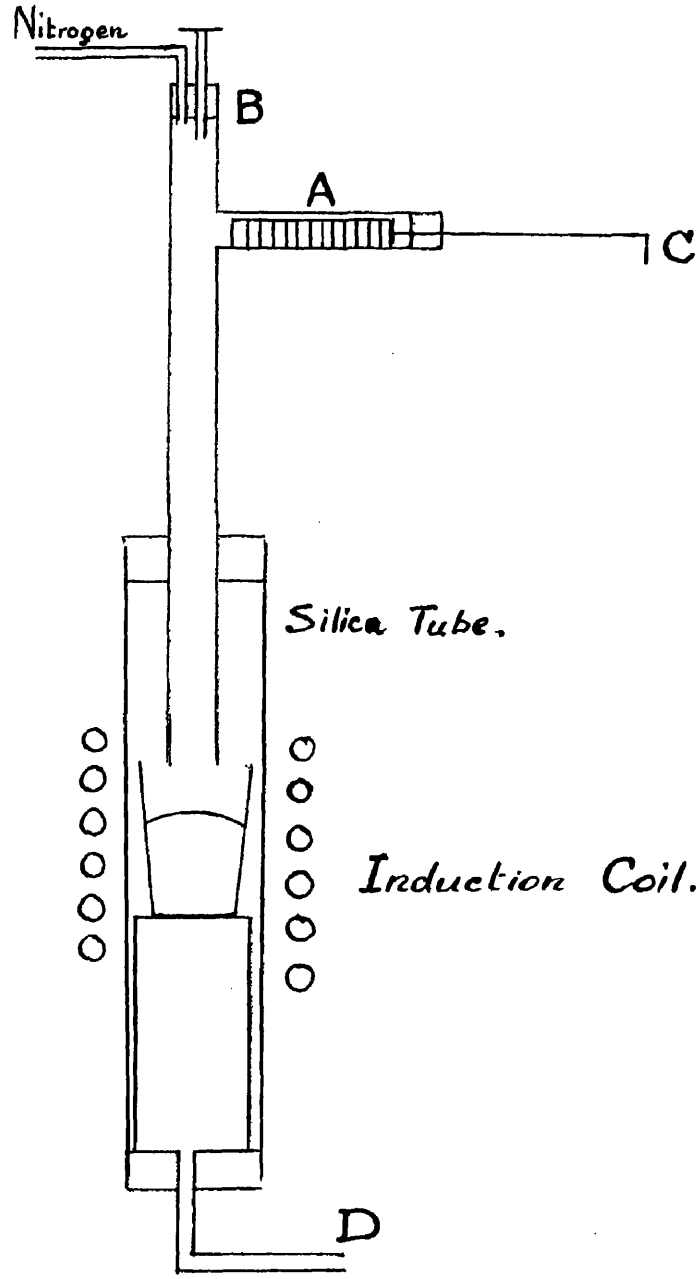


FIG. 23.

2. Crucibles.

Slip-cast fused magnesia crucibles were used, and made as described in Chapter 3. The crucibles were one inch in diameter and two inches long.

3. Furnace.

Experiments were carried out in a molybdenum furnace. This furnace has the disadvantage, however, that the winding requires a reducing atmosphere at temperatures over 500°C., to prevent the oxidation of molybdenum, and for this purpose it is usual to have another furnace in which ammonia is decomposed over iron at 700°C., into hydrogen and nitrogen. An attempt was made to eliminate the use of a second furnace and gas purification apparatus by surrounding the winding with carbon, as shown in Figure 24. The winding itself was covered by a thick layer of alundum cement, to prevent carburisation of the molybdenum wire.

Originally carbon granules were employed, but after failure due to oxidation of the wire, activated charcoal was substituted at the ends of the winding tube, to a distance of three inches. This substitution was made as the carbon granules were considered to be not sufficiently reactive to prevent oxidation of the winding during the early heating period and the final stages of cooling. The use of activated charcoal, however, was only partially successful - oxidation again occurring near both ends of the winding, after ten experiments had been carried out at 1550°C.

Although the winding life is bound to be limited by carburisation of the wire caused by carbon diffusion through the alundum layer, it is probable that this method would be more successful if the end temperatures

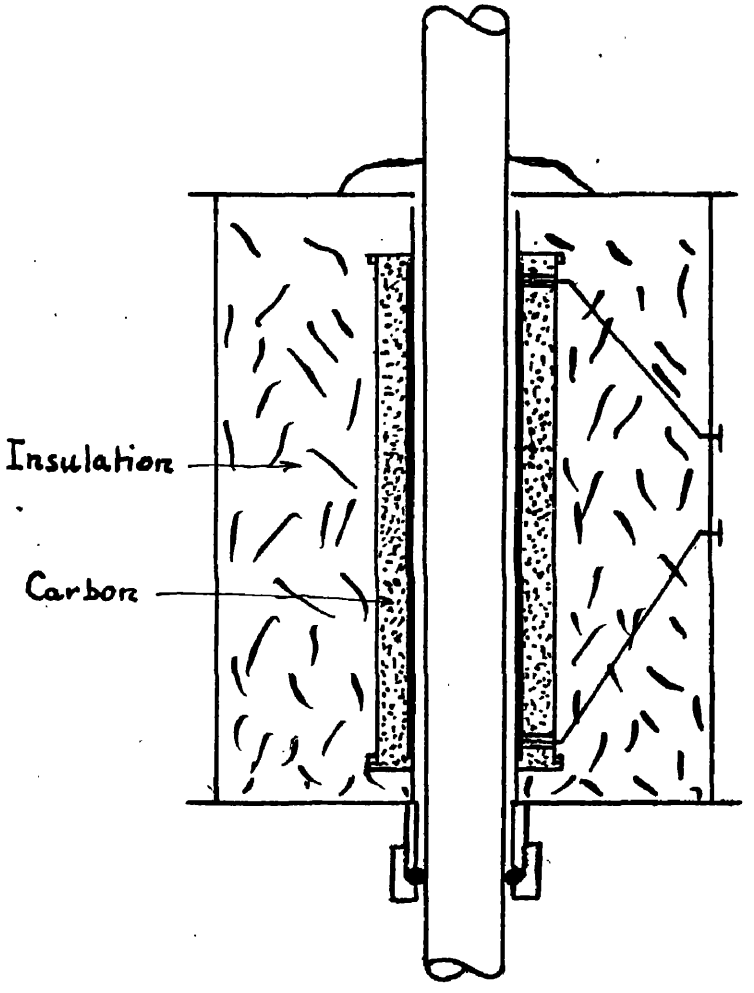


FIG. 24.

were kept over 600°C. It is estimated that this would be achieved if the furnace hot zone were maintained at a temperature greater than 1000°C. The magnesia crucibles used, however, showed poor resistance to thermal shock so that it was necessary to cool the furnace to room temperature before charging a new crucible, and for this reason it was decided to revert to the use of cracked ammonia and the furnace design used is shown in Figure 25. The furnace consisted of a metal case, 16 inches in diameter and 18 inches long, welded to the base plate and bolted firmly to the top plate, with openings at each end for the insertion of a"2 inch ΔH5" mullite furnace tube. Within the case were

(a) an outer tube, which isolated the layer of insulating brick from the crushed alumina,

(b) an inner tube, wound spirally with molybdenum wire to a distance of 15 inches to give a hot zone of ±5°C, 2·5 inches long.

Each end of the furnace was rendered "gas-tight" through the use of glands packed with asbestos rope. The bottom gland (shown in Figure 26) consisted of a screw type, and was tightened so that the mullite tube was held firmly in position, while the upper gland was made from two circular plates, machined as shown in Figure 27, and held together by four bolts, so that the entry of air was prevented, but allowing for movement of the mullite tube when expanding and contracting.

The furnace atmosphere of hydrogen and nitrogen was prepared by passing ammonia over iron turnings at 700°C., and then through concentrated sulphuric acid and anhydrous calcium chloride. The gas was introduced

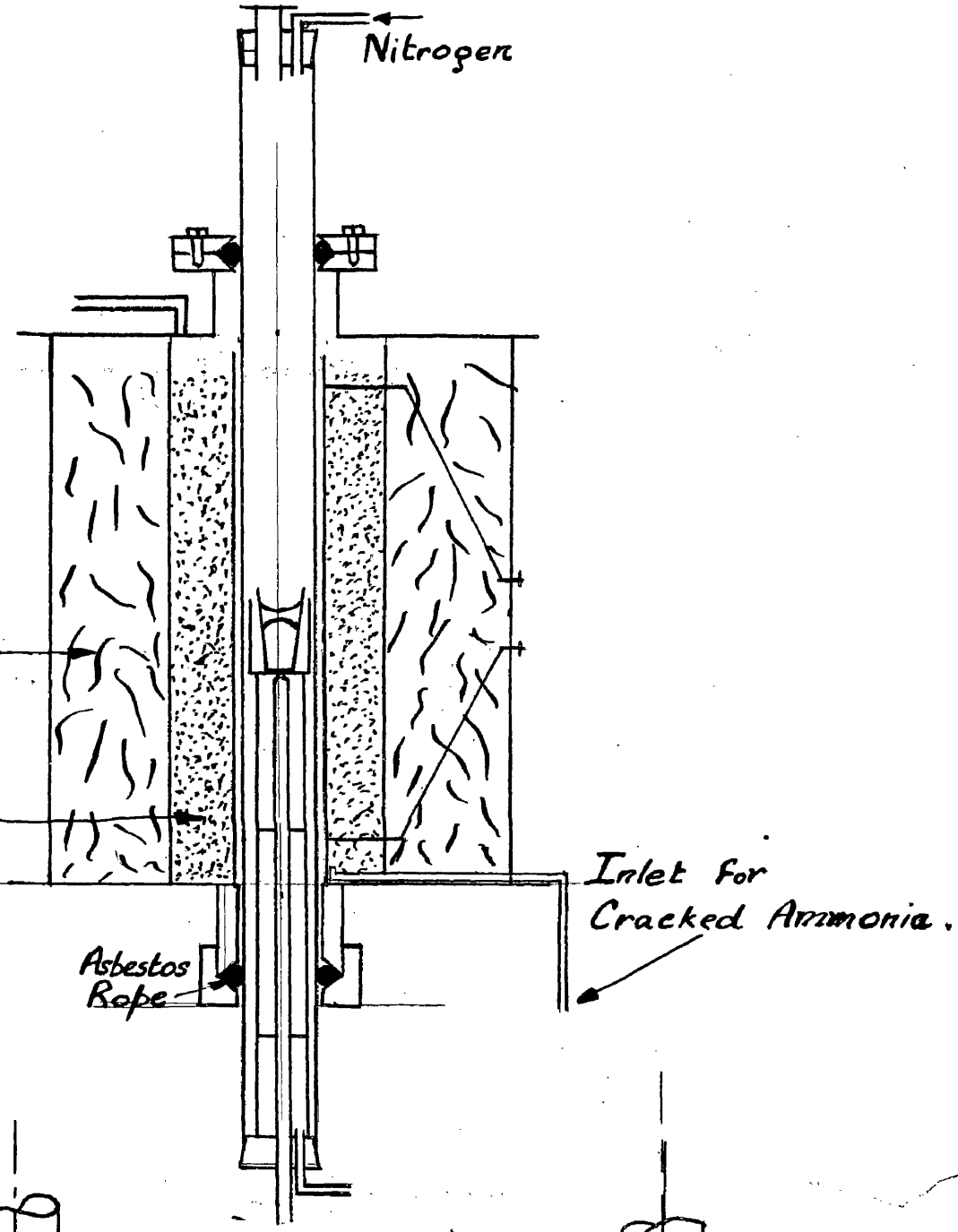


FIG. 25.

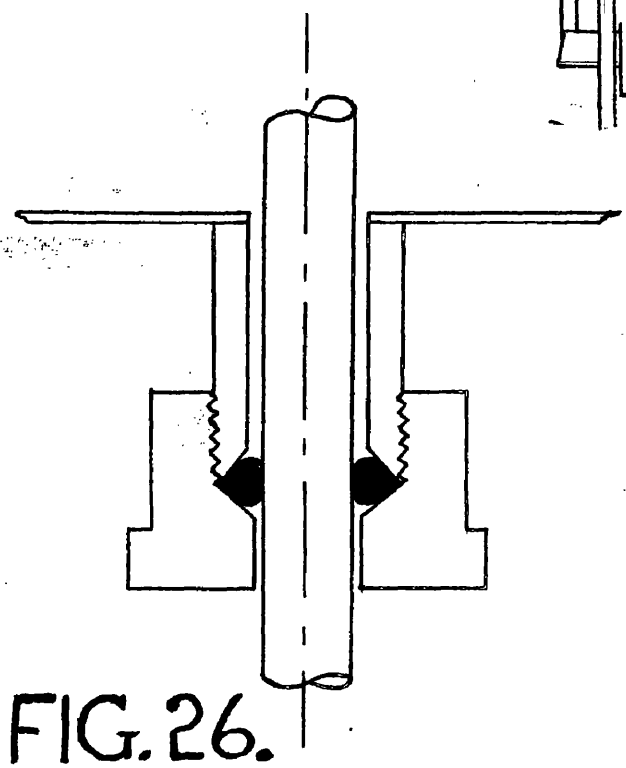


FIG. 26.

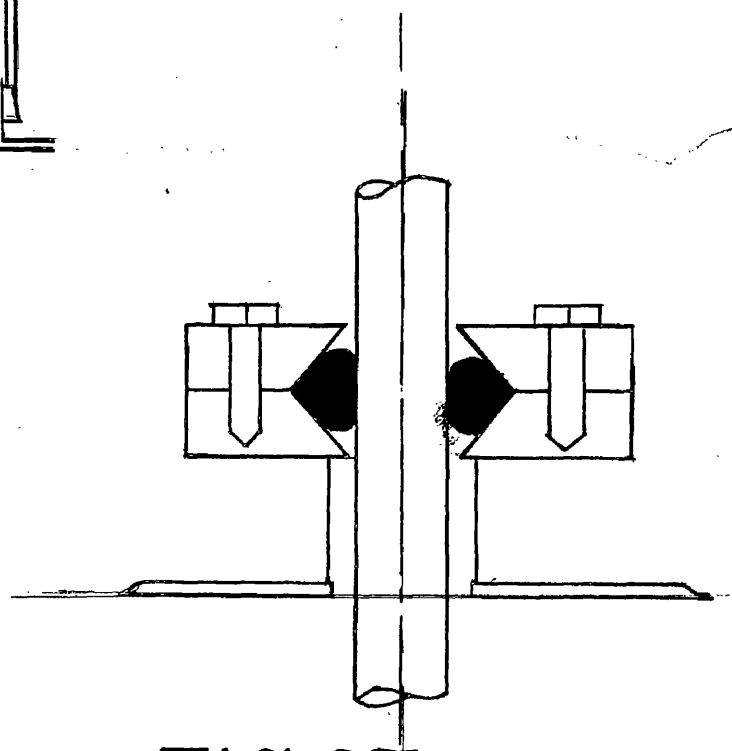


FIG. 27.

through the side of the case by a pipe which extended to the foot of the winding.

Using this design it was possible to work with a gas pressure of five inches of water, but in order to minimise the diffusion of hydrogen through the mullite at high temperatures, experiments were carried out with a pressure of less than 0.5 inches water gauge inside the case.

B. Melting Technique.

Approximately eighty grams of iron, to which was sometimes added a small amount of iron-phosphorus master alloy, when it was desired to approach equilibrium through dephosphorisation of the metal, were placed in a magnesia crucible. This was inserted into the furnace and melted in an atmosphere of pure dry nitrogen. The nitrogen was purified in the same way as described in Part I. . The furnace temperature was maintained constant at the working temperature through the use of two-20 amp. Variac transformers, which were ganged together to give an output of 40 amps.

About twenty grams synthetic slag were prepared by mixing ferrous oxide, lime, and calcium phosphate in the desired proportions, and added to the charge when the metal was molten. This practice was adopted to prevent crucible attack by the slag mixture while the metal was still solid. Slag attack on the crucible was further reduced by adding a small amount of magnesia to the synthetic slag mixture.

C. Temperature Measurements.

These were made, using a Tinsley potentiometer, and a platinum-thirteen per cent rhodium, platinum-rhodium thermocouple, which was located at the base of the crucible and had been previously standardised with gold and palladium by the bridge method. All experiments were carried out at 1550°C and a check on the accuracy of the thermo-couple readings was made by observing through the window, the melting temperature of the Armco iron in the charge.

D. Sampling.

Both slag and metal were sampled at the working temperature. The slag sample was obtained by touching the surface with a clean mild steel rod, thereby forming a chilled layer of slag on the end of the bar. The metal was sampled by suction into a silica tube, using an aspirator bulb. The sample was then rapidly quenched in water, dried and retained for the determination of phosphorus, oxygen and nitrogen.

E. Analytical Methods.

1. Slag.

Each slag sample was analysed for silica, lime, magnesia, phosphorus pentoxide and oxides of iron (Fe^{++} and Fe^{+++}).

(a) Silica. One gram of slag was dissolved in dilute hydrochloric acid, taken to dryness and baked in order to dehydrate the silica. After adding dilute hydrochloric acid the silica was filtered off and estimated as silica in the usual way.

The residue, after fuming with hydrofluoric acid, was dissolved in dilute hydrochloric acid and added to the filtrate from the silica estimation. This solution was diluted to 250 c.c. and aliquot proportions taken for the determinations of all the remaining constituents, except for ferrous iron (Fe++).

Lime and magnesia were isolated from the oxides of iron and phosphorus pentoxide, by the basic acetate separation. When the ratio of ferrous oxide to phosphorus pentoxide was less than ten to one, more iron (in the form of ferric chloride) was added to the solution, to increase the iron concentration to the proper excess.

(b) Lime. This was precipitated by 10 per cent ammonia solution (from the filtrate obtained from the basic acetate separation) as calcium oxalate, at a pH. of 6, and at 60-70°C., using methyl red as an indicator. The precipitate was allowed to stand for one hour and then filtered through gooch asbestos, washed and titrated against standard potassium permanganate solution to a pink end point.

(c) Magnesia. Magnesia was precipitated from the filtrate obtained from the lime estimation, by concentrated ammonia solution in the presence of ammonium phosphate, as magnesium ammonium phosphate. The indicator used was again methyl red. The precipitate was allowed to stand overnight, filtered, ignited to 700°C., and weighed as magnesium pyrophosphate.

(d) Phosphorus Pentoxide. The residue obtained from the basic acetate separation was dissolved in dilute nitric acid and the phosphorus pentoxide precipitated with ammonium nitro-molybdate solution(59) at 45°C. After standing for one hour, the precipitate was filtered through a sintered

glass crucible of porosity 4, washed, dried at 110°C for two hours, and weighed as ammonium phospho-molybdate.

(e) Oxides of Iron. The "total iron" content was estimated by taking a proportion of the original solution, and carrying out the normal stannous chloride reduction method, using standard potassium dichromate solution, and sodium diphenylamine sulphonate as indicator.

In estimating the "ferrous iron" present, a separate slag sample was dissolved in dilute hydrochloric acid in a carbon dioxide atmosphere. When cold, the solution was titrated against standard potassium dichromate solution using sodium diphenylamine sulphonate as an indicator.

2. Metal.

(a) Phosphorus. The metal sample was dissolved in dilute nitric acid, and the phosphorus precipitated as ammonium phospho-molybdate. After standing for one hour, the precipitate was filtered through gooch asbestos, washed thoroughly and dissolved in excess standard sodium hydroxide solution. The excess sodium hydroxide was then back titrated with standard sulphuric acid solution, using phenolphthalein solution as an indicator.

(b) Oxygen and Nitrogen. Determinations of these elements were made in a vacuum fusion apparatus which was identical with that described by Murad(60). This method is based on the affinity of carbon for oxygen, and its ability to decompose oxides at high temperatures, with the formation of carbon monoxide, and carbon dioxide. In order to achieve total reduction it was necessary to carry out the determinations at a high temperature, and also to remove the gaseous products of the reaction as quickly as possible. The

working temperature and pressure were therefore of the order 1550°C and 5×10^{-5} mm. mercury respectively.

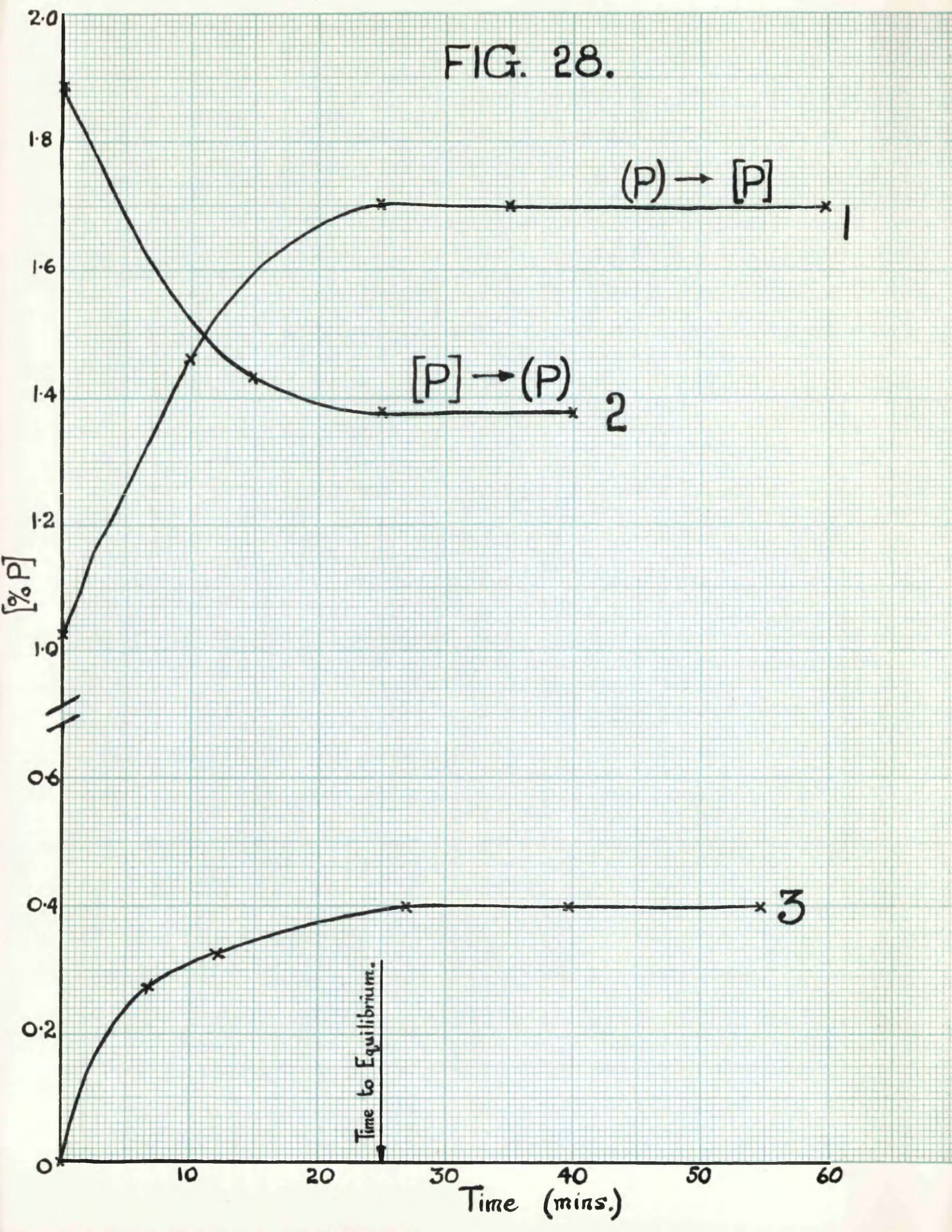
The working crucible was made of graphite, which was induction heated and insulated by -200 mesh graphite powder. An important factor in the working of the apparatus, is that the "blank" at the operating temperature should be as low as possible. It was therefore necessary to degas the crucible and the surrounding graphite powder at 2000°C for four hours, before lowering the temperature to 1550°C. A blank was then drawn for a period of half an hour and found to be of the order of 0.2 cc. per hour, and to contain approximately 33 per cent carbon monoxide. Because of the small capacity of the diffusion pump, the weight of each sample was adjusted so that all the gas evolved could be pumped off in a quarter of an hour. The average weight of the sample was therefore about two grams.

It was found that, as the phosphorus content of the metal in the graphite crucible increased, so also did the working pressure in the furnace tube. The cause was thought to be the vaporisation of phosphorus and in order to minimise this effect the phosphorus concentration was reduced by dropping phosphorus free iron, before any determinations were made.

The gas evolved from each sample was collected over mercury and then analysed in the Ambler gas analysis apparatus(61).

Analysis showed the gas to contain only nitrogen and carbon monoxide; no free oxygen or carbon dioxide was detected. The oxygen content of the metal was calculated from the volume of carbon monoxide in the gas and the nitrogen was obtained from the volume remaining after absorption with ammoniacal cuprous chloride solution.

FIG. 28.


2·0
1·8
1·6
1·4
1·2
1·0
0·6
0·4
0·2
0
[% P]
(P) → [P]
1
[P] → (P)
2
3
Time to Equilibrium.
10
20
30
40
50
60
Time (mins.)

F. Establishment of Equilibrium.

Before any reliable data could be obtained from experiments on slag-metal equilibrium, it was necessary to determine the time required to reach equilibrium. This was done by sampling the metal when the temperature reached 1550°C., and again after known time intervals. The samples were then analysed for phosphorus and when the phosphorus content was plotted against time, it was found that equilibrium was reached in 25 minutes (plots 1 and 2 in Figure 28).

It would appear from the plots that the time required to establish equilibrium between metal and slag was independent of the direction from which equilibrium was approached, i.e., either by reduction of the phosphate by iron, or oxidation of the phosphorus into the slag.

The results compare with 12 minutes, as reported by Winkler and Chipman(37), who used a radioactive calcium phosphate, and 15 to 20 minutes by Fischer and Vom Ende(40). In both these investigations, high frequency heating was employed, and this would account for the shorter times required to attain equilibrium. Quarrell and co-workers(35), whose arc-melting technique was more comparable with that adopted in the present investigation, found that the time required to attain equilibrium exceeded 20 minutes and this accounted for their maintaining a constant temperature for 40 minutes.

Since the lime-ferrous oxide-phosphorus pentoxide ternary system contained an immiscibility loop, which occurred at compositions likely to be used in slag-metal experiments, it was also necessary to investigate the effect of a heterogeneous slag layer on the rate of attainment of equilibrium with the metal. Under these conditions three liquid phases would be

present, and equilibrium would be governed by two interfacial reactions - one between the metal and the lower slag layer and the other between the two slag layers. The results are shown in plot 3 in Figure 28, where it can be seen that no difference in time was required, so that it can be assumed that of the two interfacial reactions, the metal-slag reaction is the slower. This is understandable as larger concentration gradients should occur in the metal than in each slag layer, on account of the relative volumes of the three phases taking part.

G. Results.

The results of all the slag-metal experiments carried out are shown in Table 5, where the slag analysis is expressed in weight and molar percentages and the metal analysis in weight percentages. In calculating the molar percentages the silica contents have been ignored because of the small amounts present, and the oxides of iron have been converted to (ΣFeO).

TABLE 5.

Slag No.	Time (mins.)	Slag Analysis (wt.per cent.)							Slag Analysis (Mole per cent)				Metal Analysis.		
		SiO_2	CaO	P_2O_5	FeO	Fe_2O_3	ΣFeO	MgO	CaO	P_2O_5	ΣFeO	MgO	P	O	N
3	45	0.7	23.0	42.9	N.D.	N.D.	15.6	18.0	29.8	21.9	15.7	32.6	1.350	0.075	0.039
4	30	1.0	26.2	39.6	N.D.	N.D.	16.9	16.5	33.6	20.1	16.8	29.5	1.180	0.101	0.0406
5	60	0.5	20.0	39.5	N.D.	N.D.	26.2	14.0	26.4	20.7	26.9	25.9	0.876	0.108	0.0685
6*	50	0.7	9.0	24.4	N.D.	N.D.	56.0	11.0	11.6	12.4	56.1	19.8	1.010	0.133	0.0252
7	45	0.2	5.4	31.0	45.5	4.9	50.0	14.6	7.9	15.8	50.3	26.8	1.070	0.101	0.0286
8*	60	0.7	3.5	16.0	N.D.	N.D.	67.0	14.3	4.3	7.8	63.4	24.6	1.274	0.163	N.D.
9*	60	0.5	5.3	6.4	N.D.	N.D.	84.8	4.2	6.6	3.2	82.7	7.5	0.560	0.155	0.0262
10*	50	0.5	1.9	4.8	82.5	6.0	87.9	5.5	2.3	2.4	85.6	9.5	1.015	0.161	0.0315
11	50	0.4	1.7	1.9	84.1	9.1	93.0	3.8	2.1	0.9	90.2	6.6	0.724	0.180	0.0302
12*	55	1.0	2.6	15.5	67.5	2.2	69.5	9.8	3.4	7.9	70.8	18.0	0.421	0.165	N.D.
13*	55	0.8	3.7	4.3	77.2	10.2	86.5	4.9	4.6	2.1	84.6	8.6	0.253	0.153	N.D.
14*	30	0.5	4.0	4.6	77.0	8.8	84.9	6.1	4.9	2.2	82.1	10.7	0.394	0.161	N.D.
16*	40	0.7	13.5	9.8	54.3	19.0	71.9	4.2	17.0	4.8	70.7	7.5	0.144	0.167	0.0407
18*	30	1.0	27.9	34.6	N.D.	N.D.	24.3	12.0	35.8	18.0	24.1	22.3	0.381	0.161	0.0286
19*	80	0.6	3.7	14.9	50.4	17.3	66.0	13.8	5.3	7.5	63.0	24.4	1.185	0.136	0.0220
22	33	0.5	18.7	40.0	N.D.	N.D.	23.4	18.6	24.4	20.5	23.3	31.8	0.289	0.129	0.0216
23*	40	0.6	12.6	31.3	32.9	9.4	41.4	13.9	17.6	15.7	40.8	26.0	0.572	0.163	0.0316
24*	40	0.6	12.3	23.6	N.D.	N.D.	51.8	12.9	15.5	11.7	50.8	21.8	0.632	0.138	0.0299
26	45	1.0	32.0	44.5	8.7	0.8	9.5	12.0	43.4	23.8	10.0	22.8	0.294	0.075	0.0226
27	40	1.0	32.8	44.6	6.5	2.3	8.6	13.1	43.6	23.3	8.9	24.4	0.294	0.075	0.0104
28	60	0.6	7.9	15.5	N.D.	N.D.	67.5	9.3	9.9	7.7	66.0	16.3	0.285	0.145	0.0261

TABLE 5.(CONTINUED)

Slag No.	Time (mins.)	Slag Analysis (Wt. per cent).							Slag Analysis (Mole per cent).				Metal Analysis.		
		SiO_2	CaO	P_2O_5	FeO	Fe_2O_3	ΣFeO	MgO	CaO	P_2O_5	ΣFeO	MgO	P	O	N
30	50	0.8	5.9	29.8	36.0	10.8	45.8	16.8	7.7	15.3	46.4	30.6	0.691	0.124	0.0310
31*	70	0.5	39.4	42.4	N.D.	N.D.	11.9	6.8	52.7	22.3	12.3	12.7	0.173	0.141	0.0261
32*	50	1.0	40.5	41.7	N.D.	N.D.	10.2	6.8	54.5	22.0	10.7	12.8	0.246	0.114	0.0247
35	40	0.5	18.2	44.0	16.6	3.2	19.5	18.5	23.7	22.6	19.8	33.1	1.370	0.109	0.0180
36*	30	1.0	10.6	25.1	N.D.	N.D.	51.8	11.5	13.1	12.3	54.6	20.0	0.914	0.145	0.0259
37*	30	0.9	17.9	20.9	N.D.	N.D.	49.5	11.6	22.2	10.2	47.5	20.0	0.193	0.139	0.0218
38*	35	1.0	4.2	2.3	N.D.	N.D.	88.0	4.9	5.2	0.9	85.1	8.6	0.322	0.156	0.0205
39*	40	0.7	13.1	23.0	N.D.	N.D.	51.8	12.0	16.5	11.5	50.6	21.2	0.279	0.146	N.D.
40*	45	1.0	13.3	16.7	N.D.	N.D.	59.6	10.2	16.5	8.2	57.6	17.8	0.386	0.145	0.0259
41*	40	0.5	4.7	11.5	N.D.	N.D.	73.7	9.7	5.8	5.6	71.8	16.9	0.746	0.156	0.0279
42*	40	0.9	6.0	13.7	N.D.	N.D.	71.4	10.1	7.4	6.7	68.4	17.5	0.897	0.152	0.0390
43*	40	0.2	3.5	13.0	N.D.	N.D.	73.5	10.0	4.3	6.5	72.0	17.5	1.136	0.165	0.0367

* Denotes a mixture of immiscible layers.

CHAPTER 3.

Activities in CaO-FeO-P_2O_5 Slags.

1. Effect of Magnesia.

The treatment of slag-metal data in which magnesia was a slag constituent, has confronted many investigators in the past. In some cases magnesia and lime have been assumed to have equal dephosphorising powers, while in other cases, magnesia has been regarded as a diluent, or to be only slightly basic in character. In assessing the rôle of magnesia in the phosphorus reaction, in the presence of ferrous oxide and lime, the problem has been no less acute.

Since the ionic sizes of magnesium and iron are small compared with that of calcium, it would be expected that in the liquid state (Mg^{++} and Fe^{++}) ions would be preferentially associated with oxygen ions, rather than with the larger phosphate ion ($PO_4^{\equiv}$), and because of this similarity, magnesia might be classed with ferrous oxide in the pseudo-ternary system (ferrous oxide + magnesia)-lime-phosphorus pentoxide.

On the other hand, if the variation of ferrous oxide activity with composition in the above system is being considered, ferrous oxide and magnesium oxide may not be grouped together, since magnesia makes no direct contribution to the oxygen potential of the slag.

When the ability of the slag to form a stable phosphate is considered, it would be equally incorrect to group lime and magnesia together. Thus Bookey(39) has obtained the following values for the free energies of formation of calcium and magnesium orthophosphate

$$P_2 + \tfrac{5}{2}O_2 + 3CaO \longrightarrow 3CaO.P_2O_5 \qquad \Delta G = -537 + 0{\cdot}13T \text{ Kcal.}$$

$$P_2 + \tfrac{5}{2}O_2 + 3MgO \longrightarrow 3MgO.P_2O_5 \qquad \Delta G = -483 + 0{\cdot}13T \text{ Kcal.}$$

Hence

$$3MgO.P_2O_5 + 3CaO \longrightarrow 3CaO.P_2O_5 + 3MgO \quad \Delta G = -54 \text{ Kcal.}$$

$$K_{1550} = \frac{(\ ^{a}3CaO.P_2O_5)\ (\ ^{a}MgO)^3}{(\ ^{a}3MgO.P_2O_5)\ (\ ^{a}CaO)^3} = 4.44 \times 10^6$$

Although Bookey's data were obtained from a study of reactions in the solid state, differences in the heats of fusion would not be expected to affect greatly the result for liquid slags. It would therefore be expected that for equal activities of lime and magnesia in the liquid slag, the ratio of the activities of calcium and magnesium orthophosphates would be of the order of 10^6. This may be compared with a value of 10^4 for the relative stability of the two orthophosphates given by Flood and Grjotheim(44) who used values of 22 and 18 for log $K'_{Ca^{++}}$ and log $K'_{Mg^{++}}$ respectively, in their ionic equations for dephosphorisation, and with a value of 10^7 derived from similar equations of Turkdogan and Pearson(45).

For these reasons it was considered that in the presence of lime and ferrous oxide, magnesia neither contributed directly to the degree of oxidation of the slag, nor appreciably to the lowering of the activity of phosphorus pentoxide in it. Magnesia was therefore treated as a diluent, and the slag compositions were recalculated to ($FeO+CaO+P_2O_5$) = 100 mole per cent.

It should be noted, however, that it is realised that certain slag compositions contained as much as 30 per cent (mole) of magnesia (Table 5), in which cases it is probable that magnesia would have the apparent effect of acting as an acid, through diluting the slag and so reducing the activities of lime and ferrous oxide present.

On the other hand, magnesia could act as a base, when the lime content was comparatively small, on account of the greater stability of magnesium orthophosphate compared with that of ferrous orthophosphate. Stability ratios of 10^6 and 10^3 have been assessed for these phosphates by Flood and Grjotheim(44) and Turkdogan and Pearson(45) respectively.

Hence it would appear, that in the phosphorus reaction the effect of magnesia depends on the slag composition and this may provide a possible reason for the great difference in opinion expressed by previous investigators concerning its importance in slag-metal reactions.

2. Activity of Ferrous Oxide.

Fontana and Chipman(62) have shown that the activity of ferrous oxide in pure iron is proportional to the concentration of dissolved oxygen in the metal. Since the activity of ferrous oxide is the same in both metal and slag when they are at equilibrium, it is possible to determine the activity of ferrous oxide in the slag from the oxygen content of the metal. In the present work, the activity of ferrous oxide was therefore calculated by dividing the oxygen concentration by the saturation value for oxygen in pure iron at 1550°C. The standard state in which the activity of ferrous oxide was unity was defined as the saturation oxygen concentration, i.e., the oxygen content of pure iron in equilibrium with pure ferrous oxide.

Various workers have tried to determine the oxygen concentration at saturation, in pure iron at different temperatures. Körber and Oelsen(63) in their experiments on the manganese equilibrium, used magnesia crucibles and plotted the oxygen partition $\left[[O]/(FeO)\right]$ between metal and slag against

temperature. From the ferrous oxide content of the slag, they calculated by proportion, the oxygen concentration in the metal, which corresponded to 100 per cent ferrous oxide, and reported a value of 0.23 per cent, for 1550°C.

Chipman and Fetters(64) using induction heating and magnesia crucibles found that the oxygen content of pure iron, varied little with contents of more than 90 per cent ferrous oxide in the slag. They, therefore, assumed oxygen saturation to have occurred in the range between 90 and 95 per cent ferrous oxide and reported 0.18 per cent oxygen as the saturation value at 1550°C. Later, Taylor and Chipman(49) succeeded in obtaining a direct measurement of the solubility of the pure oxide. For this purpose they used a rotating induction furnace in which the molten metal formed a cup, which retained the pure ferrous oxide uncontaminated by the crucible. Hence they obtained

$$\log[O] = \frac{6,320}{T} + 2{\cdot}734$$ where T was expressed in degrees Absolute, and [O] as a weight percentage. This equation showed oxygen saturation at 1550°C to be 0.185 per cent, which agrees with recent determinations carried out by Fischer and vom Ende(65).

In an experiment made during the course of this investigation, a value of 0.19 per cent was obtained. This is in good agreement with the results of Chipman and co-workers, and for the purposes of this investigation the equation of Taylor and Chipman for oxygen solubility in molten iron has been used. This equation, is strictly only applicable in the absence of alloying elements, as these may alter the activity coefficient of dissolved oxygen in the iron. Marshall and Chipman(66) have reported that

carbon reduces the activity coefficient of oxygen, while silicon has recently been shown by Gokcen and Chipman(67) to have a similar effect.

The mutual effects of phosphorus and oxygen when dissolved in molten iron have been investigated by Pearson and Turkdogan(55) and Richardson and co-workers(57), but only at low oxygen activities similar to those found under open hearth steelmaking conditions. For molten iron in equilibrium with lime-ferrous oxide-phosphorus pentoxide slags it is possible for oxygen and phosphorus to be present in much greater quantities. Some uncertainty therefore exists as to whether the results of Pearson and Turkdogan(55) can be applied to the data obtained in this investigation, as the mutual effects could be quite different at high oxygen activities. For the want of further data, however, oxygen activities have been calculated using Pearson and Turkdogan's(55) equation,

$$\log f_O^P = -0.032[P]$$

Table 6 shows the ferrous oxide activity values obtained from the oxygen content of the metal, after this correction for phosphorus has been applied.

As one end of the immiscibility loop lies very close to the ferrous oxide corner of the ternary system it might be expected that most compositions lying within the immiscibility loop, would have a ferrous oxide activity approaching unity. However, it will be seen from Table 6 ($a_{FeO}(l)$), that the determined values are somewhat lower, most of them having values between 0.7 and 0.8. A possible reason for this may be the presence of magnesia in the slag, and an attempt has been made to surmount this difficulty, by regarding ferrous oxide and magnesia as

TABLE 6.

Run No.	Mole % Comp. Neglecting MgO			$a_{FeO}^{(1)}$	$a_{FeO}^{(2)}$	$a \times 10^{-15}_{P_2O_5}$	$a_{CaO}^{(3)}$	$a_{CaO}^{(4)}$	$a_{CaO}^{(5)}$
	CaO	ΣFeO	P_2O_5						
3	42.2	23.3	32.6	0.37	0.42	6.0			
4	47.7	23.8	28.5	0.50	0.57	21.0			
5	35.6	36.3	28.0	0.55	0.63	19.0			
6*	14.5	70.0	15.5	0.66	0.73	53.0	0.026	0.069	0.024
7	9.3	68.9	21.6	0.50	0.57	17.2			
8*	5.7	84.2	9.5	0.79	0.86	18.8	0.017	0.045	0.021
9*	7.6	89.5	3.5	0.79	0.93	54.0	0.026	0.069	0.035
10*	2.5	94.6	2.6	0.79	0.88	134.0	0.019	0.051	0.024
11	2.2	96.7	1.0	0.91	0.98	116.0			
12*	4.1	86.5	9.6	0.85	0.93	31.0	0.031	0.083	0.042
13*	5.4	92.6	2.3	0.80	0.93	11.0	0.040	0.107	0.058
14*	5.5	92.1	2.5	0.84	0.97	33.0	0.030	0.080	0.044
16*	18.5	76.5	5.2	0.87	0.99	8.8	0.046	0.123	0.087
18*	46.1	31.0	23.2	0.83	0.91	22.0	0.034	0.091	0.045
19*	7.0	83.3	9.9	0.66	0.72	68.0	0.024	0.064	0.023
22	35.8	34.2	30.1	0.68	0.78	6.0			
23*	23.8	55.1	21.2	0.84	0.96	66.0	0.024	0.064	0.035
24*	19.9	65.0	15.0	0.71	0.82	37.0	0.029	0.077	0.033
26	56.1	13.0	30.9	0.40	0.46	0.5			
27	57.3	11.8	30.8	0.40	0.46	0.5			
28*	11.9	79.0	9.2	0.76	0.82	8.0	0.048	0.128	0.055
30	11.0	65.9	22.1	0.63	0.72	23.0			
31*	60.4	14.1	25.6	0.74	0.84	3.1	0.066	0.176	0.078
33*	62.6	12.3	25.4	0.60	0.68	2.2	0.074	0.185	0.060
35	35.9	29.9	34.2	0.54	0.62	44.			
36*	16.4	68.3	15.3	0.75	0.81	72	0.023	0.061	0.026
37*	27.8	59.5	12.7	0.73	0.81	3.3	0.065	0.170	0.071
38*	5.7	93.2	1.2	0.81	0.91	15.0	0.039	0.104	0.051
39*	21.0	64.4	14.5	0.76	0.93	13.0	0.041	0.109	0.055
40*	20.0	70.0	9.9	0.75	0.93	25.0	0.033	0.088	0.045
41*	7.0	86.4	6.8	0.79	0.87	69.0	0.024	0.064	0.030
42*	9.0	83.0	8.1	0.76	0.84	82.0	0.022	0.059	0.026
43*	5.3	87.1	7.7	0.81	0.90	187.0	0.017	0.045	0.022

* Loop Compositions within the Immiscibility loop.

(1) a_{FeO} Values obtained directly from oxygen content of metal.

(2) a_{FeO} Values corrected for effect of magnesia.

(3) a_{CaO} Values obtained from $a_{P_2O_5}$ in the slag.

(4) a_{CaO} obtained from thermodynamic data of Richardson and co-workers.

(5) a_{CaO} Values obtained from a_P in the metal.

behaving ideally in the lower layer compositions, and calculating an oxygen content by proportion on the basis of ferrous oxide replacing all the magnesia present

$$\text{i.e.} \quad [O]_{calc.} = [O]_{obs.} \times \frac{(FeO + MgO)}{(FeO)}$$

This is a reasonable assumption as the lower layers are essentially composed of ferrous oxide and magnesia, and contain only small quantities of lime and phosphorus pentoxide. For the upper layers, and compositions outside the loop, this assumption is no longer valid on account of the high phosphorus pentoxide concentrations, but the effect of magnesia in the former could be assessed indirectly from the calculated values in the associated bottom layers. This method was inapplicable, however, to compositions outside the immiscibility gap, and in those cases the ferrous oxide activity was calculated using the same multiplying factor as that used for the nearest slag on the boundary of the immiscibility loop.

In the case of those slag compositions lying within the immiscibility loop, the actual analysed slag sample consisted of a mixture of the two layers, so that the analysis in Table 5 cannot be regarded as representative of a simple liquid phase. Two homogeneous slags in equilibrium could be computed, however, by plotting the analysed composition in the pseudo-ternary diagram, (ferrous oxide + magnesia) - lime - phosphorus pentoxide, shown in Figure 29, and reading off the top and bottom layer compositions corresponding to it. Figure 29 was constructed on a molar basis, from the results of the melts made in magnesia crucibles at 1550°C, shown in Table 7, but has the disadvantage that only the lime and phosphorus pentoxide contents could be obtained directly, the remainder being expressed

TABLE 7.

MOLE PER CENT.

Slag No.	Original Composition.			Top Layer.				Bottom Layer.			
	FeO	CaO	P_2O_5	FeO	P_2O_5	CaO	MgO	FeO	P_2O_5	CaO	MgO
13	84.4	8.1	7.5	39.4	16.2	17.0	27.4	88.3	1.2	2.4	8.1
14	74.6	15.1	10.3	34.7	18.2	24.2	22.9	86.3	0.5	2.7	10.5
15	67.1	22.3	10.7	17.5	20.3	38.9	23.3	84.0	0.5	3.7	11.8
16	46.8	40.1	13.2	7.9	22.3	59.1	10.7	76.8	0.9	12.4	10.1
17	50.6	39.1	10.3	8.6	21.9	63.8	5.7	70.9	0.7	19.6	8.6
18	48.7	43.8	7.5	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
19	43.1	49.4	7.5	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
1540° 10	49.1	43.9	8.0	14.1	18.2	62.2	5.5	67.2	1.4	24.5	6.9
1520° 11	43.5	48.6	7.9	27.0	12.8	56.6	3.6	52.2	3.7	36.3	7.8

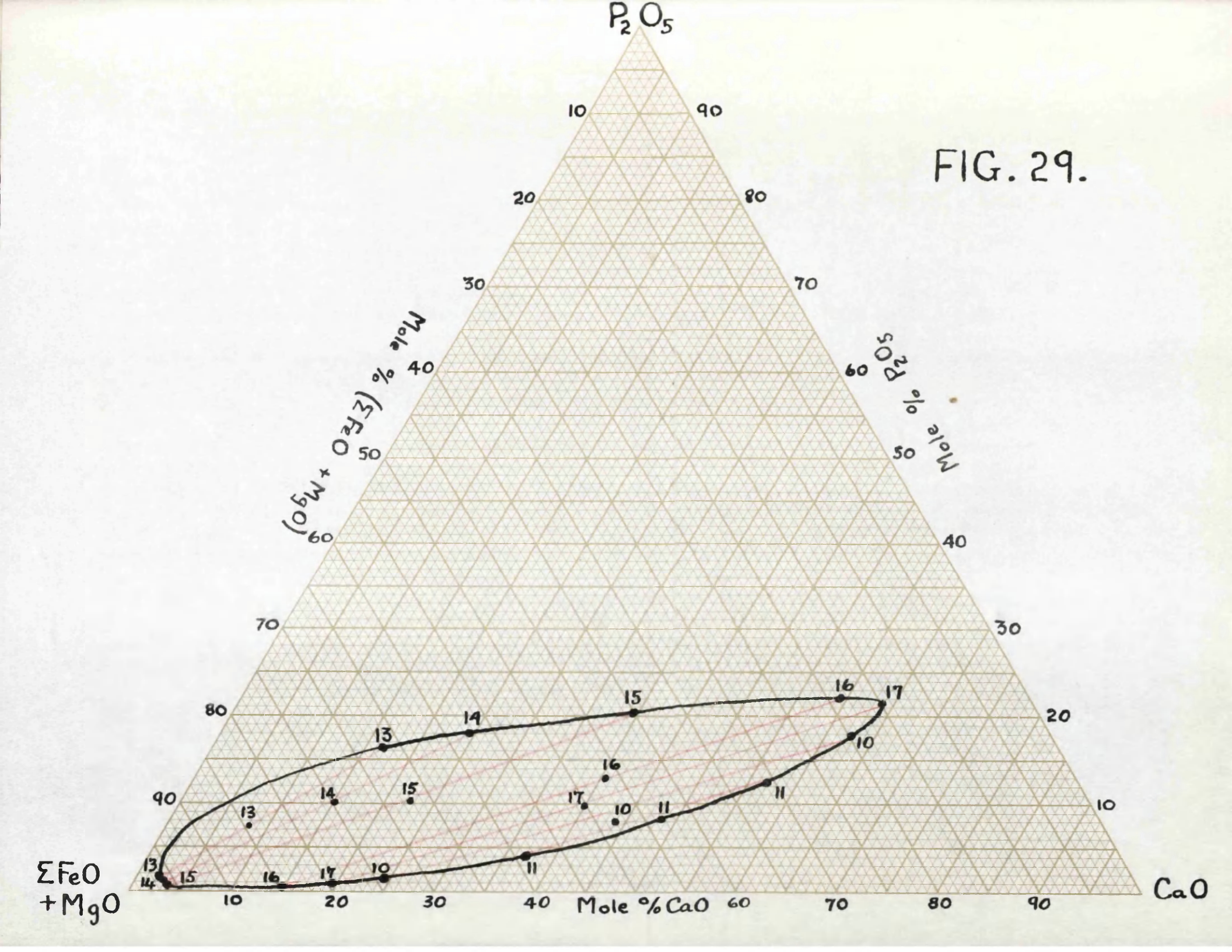

P_2O_5
10
90
20
80
30
70
40
60
50
50
60
40
70
30
80
20
90
10
(ΣFeO + MgO) % mole
P_2O_5 % Mole
ΣFeO
+MgO
Mole % CaO
CaO
10
20
30
40
50
60
70
80
90
13
14
15
16
17
10
11

FIG. 29.

as a combined value for ferrous oxide and magnesia.

The proportion of magnesia associated with the ferrous oxide was derived from the plot in Figure 30, which was constructed from the results given in Table 7. It can be seen that for compositions on the phosphorus pentoxide side of the immiscibility loop, a decrease in lime content is accompanied by an increase in magnesia pick-up, which reaches a maximum of 26.5 per cent at the nodal point, close to the ferrous oxide - phosphorus pentoxide binary system, after which the magnesia content falls rapidly as the pure ferrous oxide composition is approached. In the case of those slags on the lime-rich side of the immiscibility loop the magnesia content in the lower layers reaches a maximum value of 9.6 per cent, which then steadily decreases, with further lime additions to 3.7 per cent near the tricalcium phosphate tip of the immiscibility loop. The top and bottom layer compositions computed from Figures 29 and 30, are tabulated in Table 8 and ferrous oxide activity values corrected for the effect of magnesia are tabulated in Table 6 ($^{a}_{FeO}(2)$).

In Figure 31, the activity of ferrous oxide in the slag has been plotted against slag composition (neglecting magnesia) using the results of this investigation together with those experiments carried out below 1560°C by Fischer and vom Ende(40). It will be seen that the iso-activity curves enter the immiscibility loop, with the exception of those corresponding to less than 0.5 which follow the contour of the loop, but outside it. These have been drawn in this manner as a more rapid decrease in ferrous oxide activity would be expected on the lime-rich side of the loop, than on the phosphorus pentoxide side. The results of

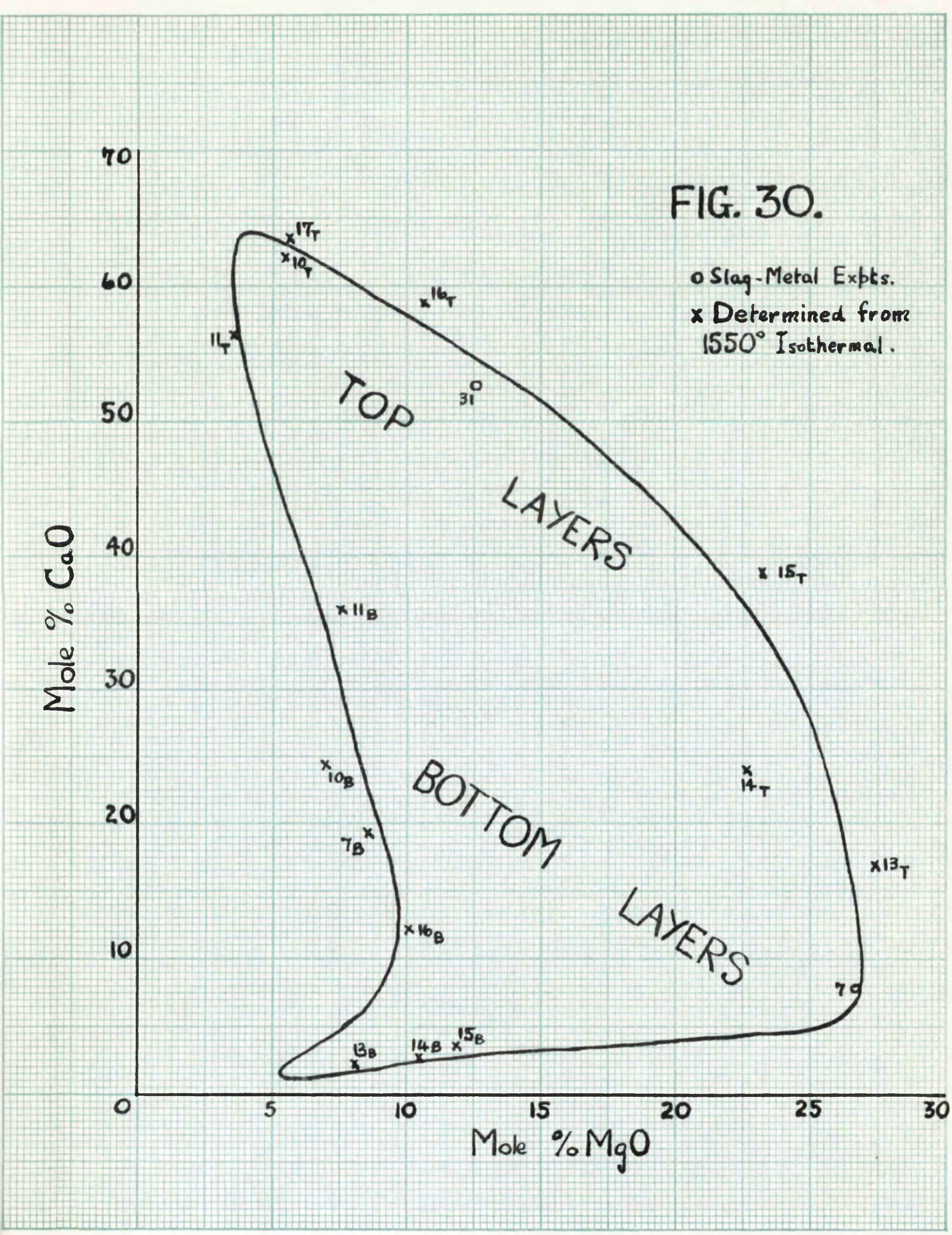
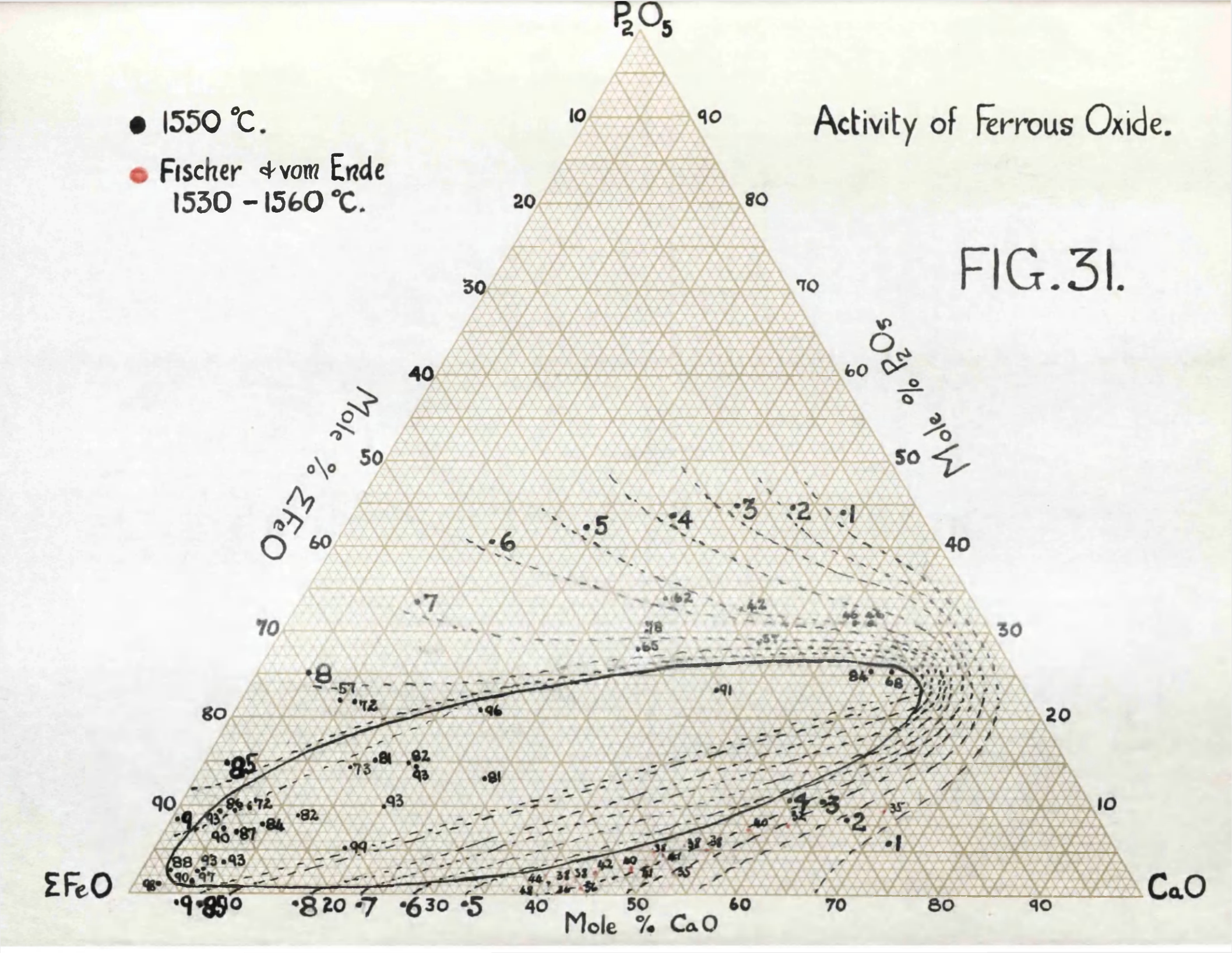


FIG. 30.
o Slag-Metal Expts.
x Determined from 1550° Isothermal.
TOP LAYERS
BOTTOM LAYERS
Mole % CaO
Mole % MgO
70
60
50
40
30
20
10
0
5
10
15
20
25
30
17T
10T
16T
11T
31
15T
11B
14T
10B
13T
7B
16B
7
13B
14B
15B

TABLE 8.

Slag	Analysed Composition (Mole per cent).				Assoc. Top Layer (Mole per cent)				Assoc. Bottom Layer (Mole per cent).			
	CaO	P_2O_5	FeO	MgO	CaO	P_2O_5	FeO	MgO	CaO	P_2O_5	FeO	MgO
6	11.6	12.4	56.1	19.8	14.5	15.5	43.3	26.7	1.9	2.0	87.6	8.5
8	4.3	7.8	63.4	24.6	7.2	12.0	53.8	27.0	1.5	3.0	89.0	6.5
9	6.6	3.2	82.7	7.5	28.5	19.0	27.8	24.7	3.0	1.0	83.5	12.5
10	2.3	2.4	85.6	9.5	12.5	15.0	45.7	26.8	1.9	2.1	87.5	8.5
12	3.4	7.9	70.8	18.0	5.0	10.2	57.2	27.6	1.4	4.5	87.4	6.7
13	4.6	2.1	84.6	8.6	26.0	19.0	29.7	25.3	2.8	1.1	83.8	12.3
14	4.9	2.2	82.1	10.7	27.0	19.1	28.9	25.0	2.9	1.1	83.5	12.5
16	17.0	4.8	70.7	7.5	53.0	22.2	10.7	14.1	10.0	0.5	80.0	9.5
18	35.8	18.0	24.1	22.3	38.9	20.3	19.0	21.8	3.7	0.5	88.7	6.8
19	5.3	7.5	63.0	24.4	9.0	13.0	51.1	26.9	1.5	2.5	89.2	6.8
23	17.6	15.7	40.8	26.0	19.9	17.5	36.4	26.2	2.8	1.2	83.9	12.3
24	15.5	11.7	50.8	21.8	24.5	18.5	31.5	25.5	2.85	1.25	83.4	12.5
28	9.9	7.7	66.0	16.3	20.8	17.6	35.5	26.1	1.2	2.6	90.7	5.5
31	52.7	22.3	12.3	12.7	52.7	22.3	10.7	14.3	10.0	0.5	80.0	9.5
32	54.5	22.0	10.7	12.8	55.5	22.5	9.8	12.2	11.5	0.5	78.3	9.7
36	13.1	12.3	54.6	20.0	16.8	16.4	40.4	26.4	2.0	1.8	88.7	7.5
37	22.2	10.2	47.5	20.0	41.9	21.2	16.4	20.5	5.1	0.6	86.6	7.7
38	5.2	0.9	85.1	8.6	41.0	21.0	17.2	20.8	5.0	0.5	86.8	7.7
39	16.5	11.5	50.6	21.2	34.0	19.5	23.1	23.4	3.0	1.0	80.0	16.0
40	16.5	8.2	57.6	17.8	36.8	20.1	20.5	22.6	3.2	0.8	78.8	17.2
41	5.8	5.6	71.8	16.9	16.0	16.0	41.5	26.5	2.0	1.8	88.4	7.5
42	7.4	6.7	68.4	17.5	15.1	13.0	45.3	26.6	2.03	1.75	88.6	7.6
43	4.3	6.5	72.0	17.5	10.2	14.0	48.9	26.9	1.8	2.2	88.0	8.0


● 1550 °C.
● Fischer & vom Ende
1530 – 1560 °C.
Activity of Ferrous Oxide.
FIG. 31.
P_2O_5
Mole % P_2O_5
Mole % ΣFeO
ΣFeO
CaO
Mole % CaO

Fischer and vom Ende appear to support this conclusion. Unfortunately the position of these isoactivity lines could not be confirmed as no experimental results could be obtained in the lime-rich part of the immiscibility loop, on account of crucible failure, caused by the highly fluid and corrosive nature of the bottom slag layer.

The scatter in the results of this investigation, especially those outside the immiscibility loop, is mainly due to the fact that the correction for the dilution of the slag by magnesia, could not be applied accurately to slags outwith the immiscibility loop. The ferrous oxide activity values for those slags are therefore less reliable than those inside the loop.

The intercepts of the iso-activity lines with the ferrous oxide-phosphorus pentoxide binary, show positive deviations. Although no quantitative data are available on the activity of ferrous oxide in this system there is every reason to expect positive deviations, on account of the shape of the ferrous oxide liquidus curve shown in Figure 10.

In the case of the ferrous oxide-lime binary system, use has been made of the results of Taylor and Chipman(49) on the activities of ferrous oxide, shown in Figure 32. These authors reported negative deviations from ideality, which they attributed to the tendency to calcium ferrite formation. Figure 32 also shows the results of the same authors' investigation on the activity of ferrous oxide in silicate melts, containing, iron, magnesium and calcium. It can be seen that when their results are plotted in the pseudo-ternary system, (lime + magnesia) - silica-ferrous oxide, a distinct break occurs in the iso-activity lines, at points along

FIG. 32.

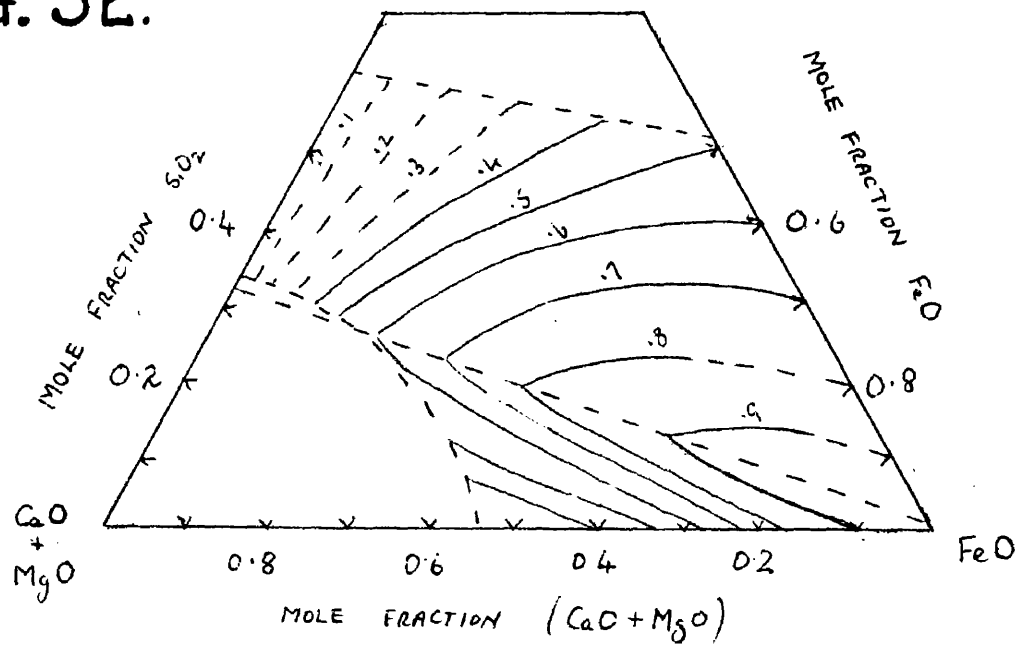
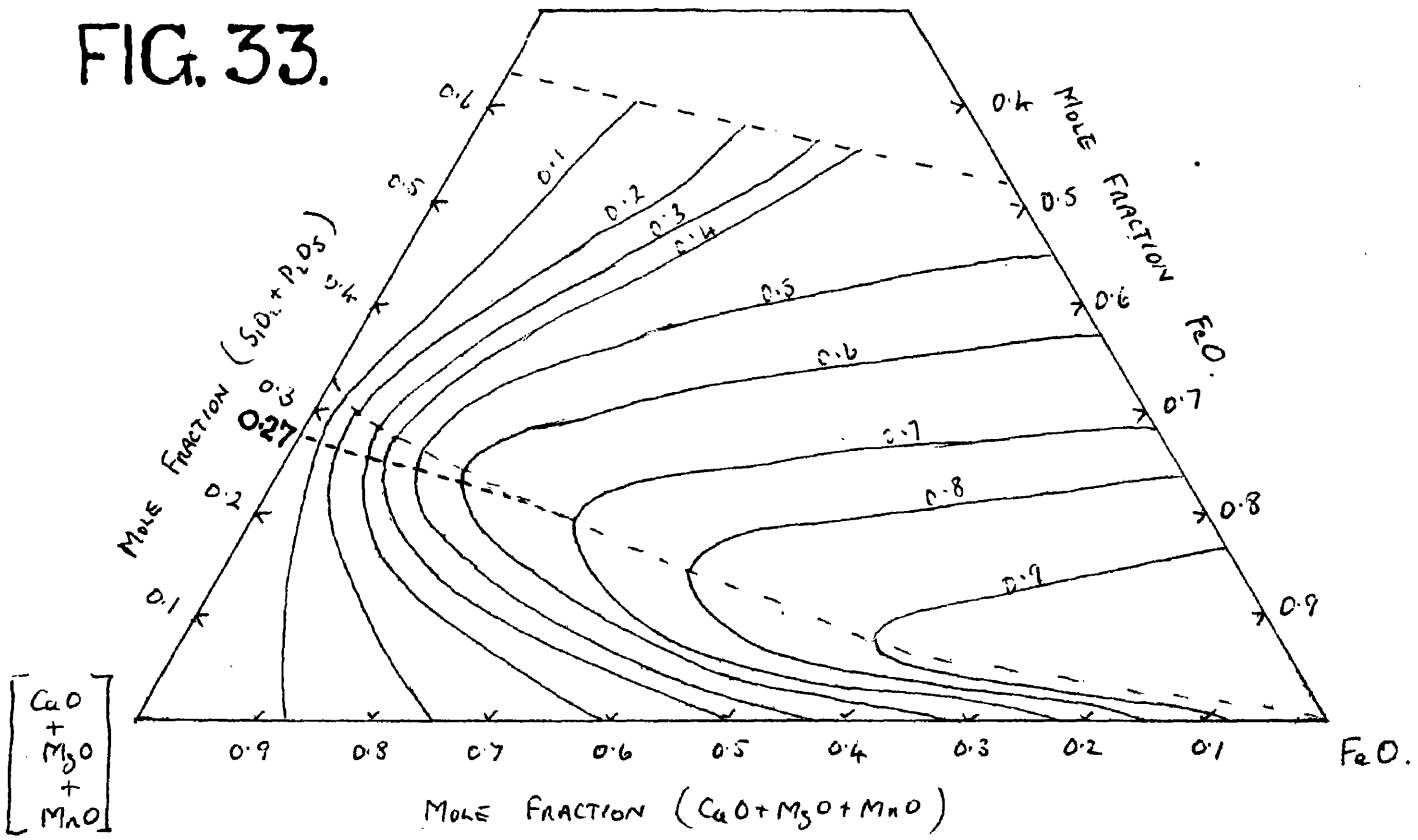


FIG. 33.



a_{FeO} Iso-activity Curves.

the line joining ferrous oxide to the ortho-silicate composition of calcium and magnesium.

From existing data Turkdogan and Pearson(50) recently extended the range covered by Taylor and Chipman, and determined the activity of ferrous oxide for compositions applicable to both acid and basic steelmaking. Their results were plotted in the pseudo-ternary system, ferrous oxide-(lime + magnesia + manganous oxide)-(silica + phosphorus pentoxide) shown in Figure 33. The isoactivity curves are located differently from those of Taylor and Chipman(49) shown in Figure 32, in that the locus of the inflexion points of these curves is not a straight line, but a curve which cuts the basic oxide - acidic oxide "binary" at a point corresponding to an approximate base:acid ratios of 2:1. On examining the curves more closely, however, the point corresponding to 27 mole per cent (SiO_2 + P_2O_5) would seem to be a more accurate intercept on this side of the diagram. There is no fundamental reason for the point of intersection to occur at the 2:1 ratio in mixed silicate-phosphate slags. This ratio in silicate slags was suggested by Taylor and Chipman(49) on the basis of a certain degree of segregation (i.e., a tendency to form two liquid layers) occurring between ferrous oxide and calcium magnesium silicates in the liquid state. The difference between the curves of Taylor and Chipman(49) and Turkdogan and Pearson(50) is due mainly to the presence of phosphorus pentoxide in the slag data examined by the latter workers. From the iso-activity curves shown in Figure 31 for the lime-ferrous oxide - phosphorus pentoxide system, it can be seen that the tips of the curves approximate to a composition of 25 mole per cent phosphorus pentoxide, 75 mole per cent

lime, so that in a complex slag, phosphorus pentoxide would have the effect of moving the locus of inflexion points of the iso-activity curves nearer the ferrous oxide - basic oxide side of the pseudo-ternary, and the amount of deviation from the 2:1 ratio could be regarded as a measure of the ratio of silica to phosphorus pentoxide in the slags.

3. Activity of Phosphorus Pentoxide.

In determining the activity of phosphorus pentoxide in the slag, use was made of recent thermodynamic data published by Turkdogan and Pearson(45) in which they reported the free energy change for the reaction

$$2[P]_{1\%} + 5[O]_{1\%} \longrightarrow P_2O_{5\,Liq.}$$

as $\Delta G = -168{,}000 + 133\ T$ cal.

If this equation is combined with

$$5(FeO) \longrightarrow 5[O] + 5Fe \qquad \Delta G = 144{,}600 - 62.55\ T \text{ cals.}$$

we obtain

$$2[P]_{1\%} + 5(FeO) \longrightarrow P_2O_{5\,Liq.} + 5Fe$$

for which $\Delta G = -23{,}400 + 70.45\ T$ cals.

Hence at 1550°C, $\log K_P = -12.59$

where $$K_P = \frac{(a_{P_2O_5})}{[a_P]^2 (a_{FeO})^5}$$

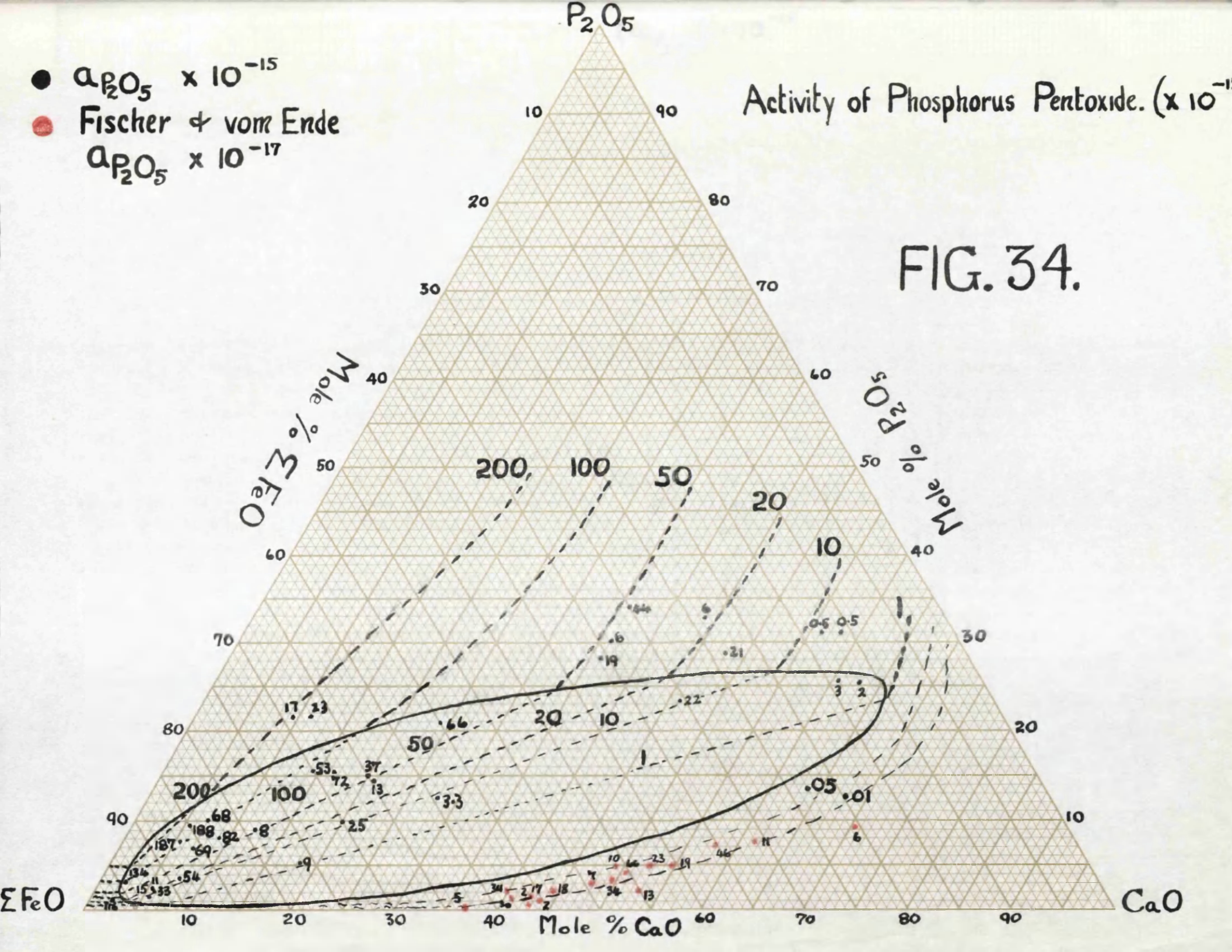
On account of the high phosphorus and oxygen concentrations encountered in the present work, the activity of phosphorus could not be assumed equal to its weight percentages, but was corrected for the mutual interaction between phosphorus and oxygen by means of the following equation:-

$$\log f^{O}_{P} = -0.062[\%O]$$

If the ferrous oxide activities given in Figure 31 are used in the above equation for log Kp, values can be calculated for the activity of phosphorus pentoxide in lime-ferrous oxide phosphorus pentoxide slags. Values so obtained are recorded in Table 6 and plotted in Figure 34.

A certain amount of scatter in the results is to be expected, since the term (a_{FeO}) enters into the calculation as a fifth power, and relatively small errors in the determination of oxygen can lead to considerable errors in the activity of phosphorus pentoxide. However, the trend in the values obtained is quite distinct, and shows that the activity of phosphorus pentoxide increases with the concentration of phosphorus pentoxide and the ferrous oxide - lime ratio in the slag. As would be expected from existing knowledge, an increase in the lime content of the slag is accompanied by a marked decrease in the phosphorus pentoxide activity. This is particularly evident when the values obtained in the present work are compared with those calculated from the results of Fischer and vom Ende(40) who used lime crucibles.

The dependence of phosphorus activity in the metal on phosphorus pentoxide activity in the slag is shown in Figure 35. It can be seen that the results for slag compositions lying within the immiscibility loop, follow a smooth curve of the exponential type, while those outwith the loop follow a much shallower curve and show greater scatter. The difference is obviously due to the higher oxygen concentrations associated with those compositions inside the immiscibility loop compared with those outside it. For a given curve or oxygen concentration level, however, it is clear that the phosphorus in the metal increases with the phosphorus pentoxide


● $a_{P_2O_5}$ x 10^{-15}
● Fischer & vom Ende $a_{P_2O_5}$ x 10^{-17}
Activity of Phosphorus Pentoxide. (x 10^{-1}
FIG. 34.
P_2O_5
Mole % P_2O_5
Mole % ΣFeO
ΣFeO
CaO
Mole % CaO
200
100
50
20
10
1
.05
.01

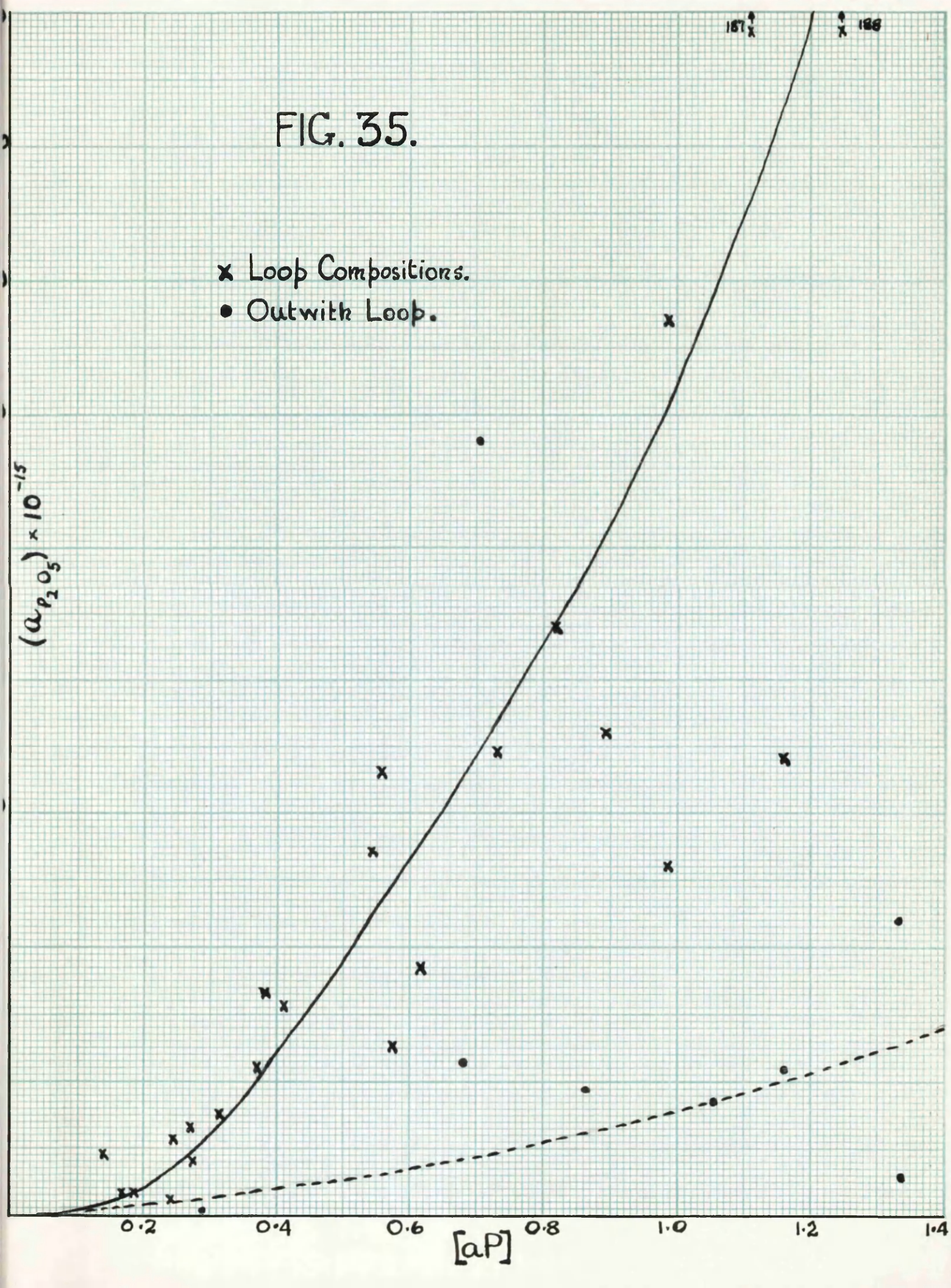


FIG. 35.
× Loop Compositions.
• Outwith Loop.
$(a_{P_2O_5}) \times 10^{-15}$
[aP]
0·2
0·4
0·6
0·8
1·0
1·2
1·4
187
188

activity in the slag.

The relation between the activites of oxygen and phosphorus in the metal is shown in Figure 36,and in the same way as in Figure 35, slag compositions within the loop show a different behaviour from those outside the loop. A more interesting fact in this case, however, is that at the higher oxygen level, the oxygen activity does not vary greatly between 0 and 1.35 per cent phosphorus. (The scatter is too great in the case of the compositions at the lower oxygen concentration level to warrant a similar assumption). The apparent mutual independence of phosphorus and oxygen concentrations in the metal, for compositions within the immiscibility loop would suggest that the activity of phosphorus pentoxide in these slags is controlled mainly by the activity of lime.

4. Activity of Lime.

The ferrous oxide activity of those slags within the immiscibility loop which have been investigated does not vary to any great extent. It would similarly be expected that over the same range of compositions the activity of tricalcium phosphate would not show great variations. (Since all the upper layer compositions examined in this work possessed CaO/P_2O_5 ratios less than 3, it seems more appropriate to consider these slags in terms of tricalcium phosphate rather than tetracalcium phosphate.) The tip of the immiscibility loop nearest to the composition of tricalcium phosphate lies in the field of crystallisation of the latter compound, and as the liquidus temperature at this point is close to 1550°C., it would appear that the activity of tricalcium phosphate along the axis of the

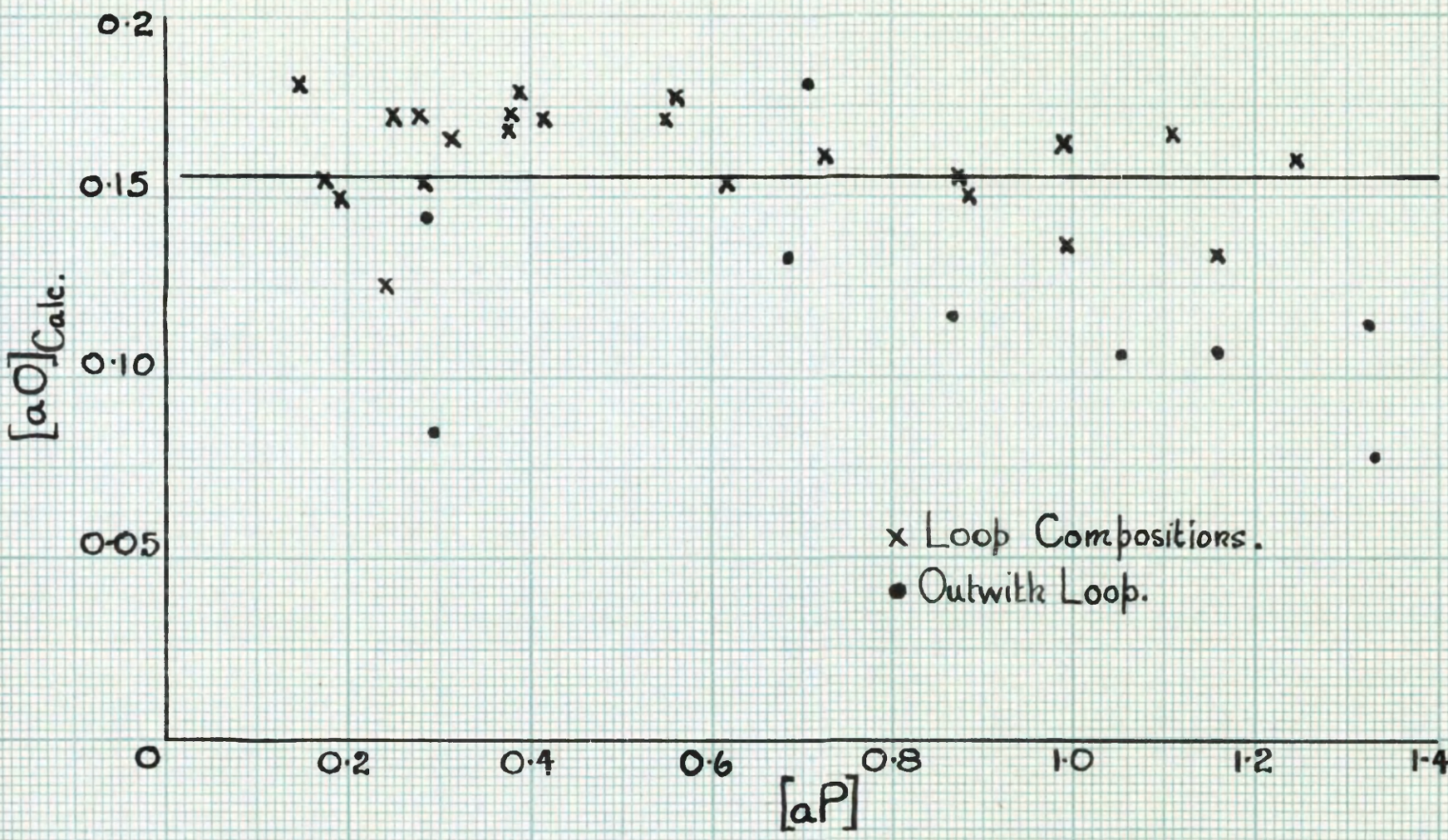

0·2
0·15
0·10
0·05
[aO]Calc.
0
0·2
0·4
0·6
0·8
1·0
1·2
1·4
[aP]
x Loop Compositions.
• Outwith Loop.

FIG. 36.

immiscibility gap, referred to solid tricalcium phosphate as the standard state, is approximately unity. It is probable that this value will not fall below about 0.9 before the nodal point in the upper half of the gap is reached. No great error should therefore be incurred if a mean value of 0.95 is taken for those slag compositions in the gap (i.e., mainly in the upper half of the gap,) which have been investigated.

Using this assumption, and with the aid of appropriate thermodynamic data (20, 39, 68-71) it is possible to calculate values for the activity of lime in these slags:

$$3CaO_s + 2\tfrac{1}{2}O_{2g} + P_{2g} \rightarrow 3CaO.P_2O_5 \quad \Delta G = -553,350 + 140T \text{ cals.}$$

$$P_{2g} + 2\tfrac{1}{2}O_{2g} \rightarrow P_2O_{5\,Liq.} \quad \Delta G = -366,750 + 121T \text{ cals.}$$

Hence

$$3CaO_s + P_2O_{5\,Liq.} \rightarrow 3CaO.P_2O_5 \quad \Delta G = -186,600 + 19T \text{ cals.}$$

At 1550°C $\Delta G = -151,360$ cals.

Hence

$$\log \frac{(a_{CaO})^3 (a_{P_2O_5})}{(a_{3CaO.P_2O_5})} = \frac{-151,360}{4.575 \times 1823} = -18.14$$

$$(a_{CaO}) = \sqrt[3]{\frac{8.88 \times 10^{-19}}{(a_{P_2O_5})}}$$

Values of (a_{CaO}) were calculated from the previously determined phosphorus pentoxide activity values. The former are included in Table 6 under $a_{CaO}(3)$.

Richardson, Jeffes and Withers(32) have reported a somewhat different free energy change for the reaction

$$3CaO_s + P_2O_{5\,Liq.} \rightarrow 3CaO.P_2O_{5\,s} \quad \Delta G^\circ_{631\text{-}1731^\circ K} = -172,800 + 18.16T \text{ cals.}$$

If the use of this equation is extended to 1550°C

$$\Delta G^{\circ}_{1823^{\circ}K} = -139{,}700 \text{ cals.}$$

This leads to (a_{CaO}) values (included in Table 6 as $a_{CaO}(4)$) almost three times those calculated above. However, in each case the uncertainty in the free energy data is ± 10 kcals., so that each value is almost within the limits of error of the other.

An approximate indication as to which of these two sets of a_{CaO} values is more likely to be correct may be obtained by making use of the results of a slag metal experiment carried out in a tri-calcium phosphate crucible at 1600°C., by Trömel and Oelsen(25). Their upper and lower layer compositions have already been plotted in Figure 11 as slag 12, and the equilibrium concentration of phosphorus in the metal was reported as 0.086 per cent. Since the present investigation was carried out at 1550°C., it was necessary to calculate the equivalent phosphorus concentration at this temperature, and for this purpose the temperature relation of Fischer and vom Ende(40) was used, since it was determined from slag-metal data relating to the same ternary system.

$$\log K'' = \log \frac{1}{[P]^2[O]^5} = \frac{53{,}000}{T} - 19.4$$

Although the concentration of oxygen in the metal was not reported, the effect of the small temperature difference was accounted for by using the saturation values at 1550° and 1600°C. (This is equivalent to assuming that a_{FeO} for a given slag does not vary appreciably with temperature. It would probably be more correct to assume that $\log \gamma_{FeO}$ was a linear function of $\frac{1}{T}$, but the correction so calculated is small,

as has already been shown to be the case by Turkdogan and Pearson(50)). Hence,

$$\frac{\log K''_{1600}}{\log K''_{1550}} = \frac{\log [\text{O sat.}]^5_{1550} [P]^2_{1550}}{\log [\text{O sat.}]^5_{1600} [P]^2_{1600}}$$

and $$[P]_{1550} = 0.056 \text{ per cent.}$$

The activity of phosphorus pentoxide in the slag was obtained from Figure 35 as that which would be in equilibrium with a phosphorus activity of 0.056 per cent, and was found to be 2×10^{-16}. On substituting this value for the activity of phosphorus pentoxide in the equation,

$$a_{CaO} = \sqrt[3]{\frac{8.89 \times 10^{-19}}{(a_{P_2O_5})}}$$

(again assuming the activity of tri-calcium phosphate to be 0.95) the activity of lime in Trömel and Oelsen's slag was found to be 0.155. Since the activity of phosphorus in the metal has been found to be approximately independent of the oxygen content for slags within the immiscibility loop,

$$[P]^2 \sim \propto \frac{1}{(a_{CaO})^3}$$

so that at 1550°C

$$(0.056)^2 = \frac{K}{(0.155)^3}$$

and $$K = 1.168 \times 10^{-5}$$

This value of K was used to calculate values of a_{CaO} for different phosphorus concentrations and the results obtained are plotted in Figure 37. Using the corresponding metal phosphorus content, the activity of lime for any slag composition was then read off from Figure 37. These values are recorded in Table 6 as $a_{CaO}(5)$. It can be seen that these values agree

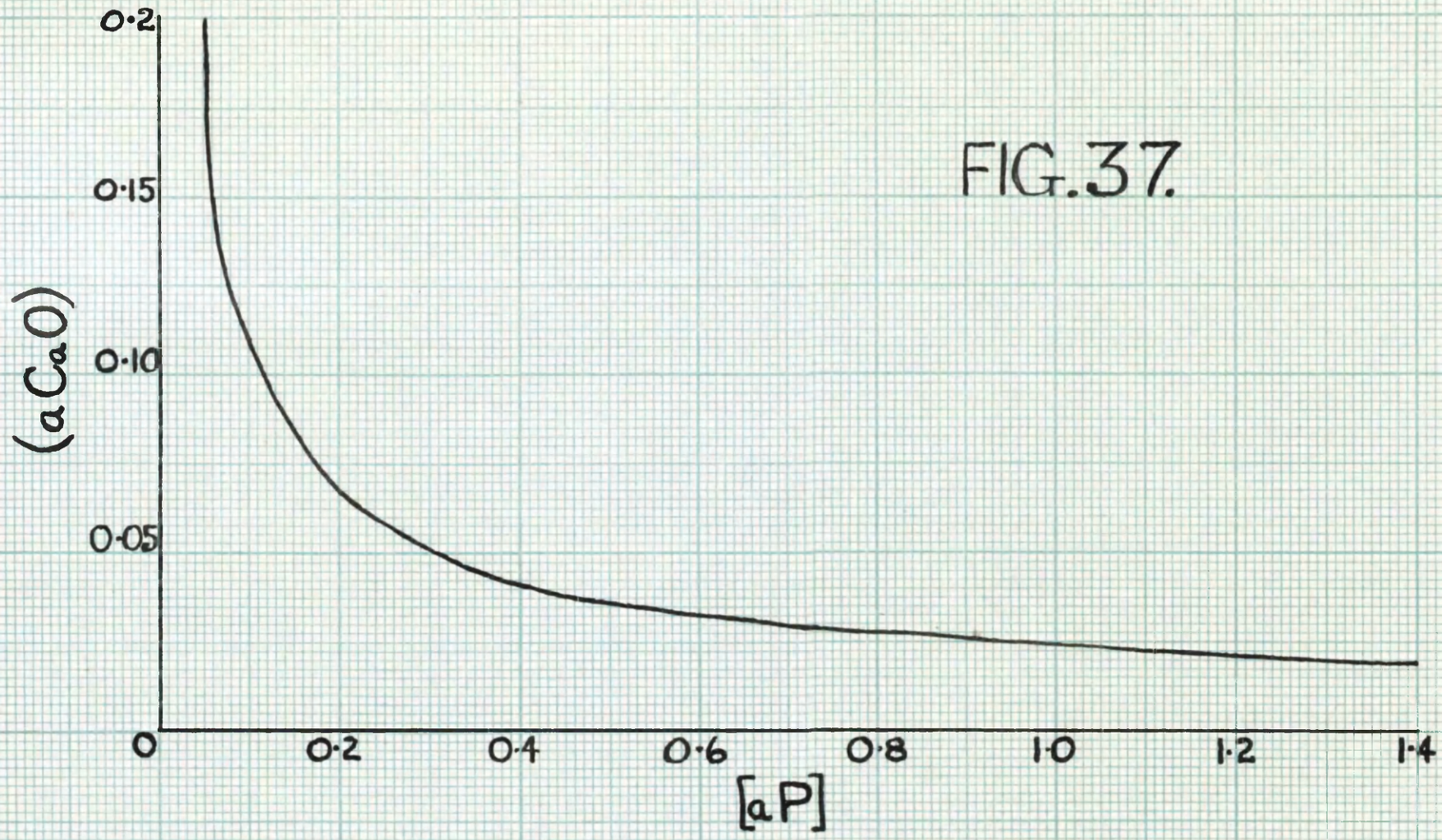
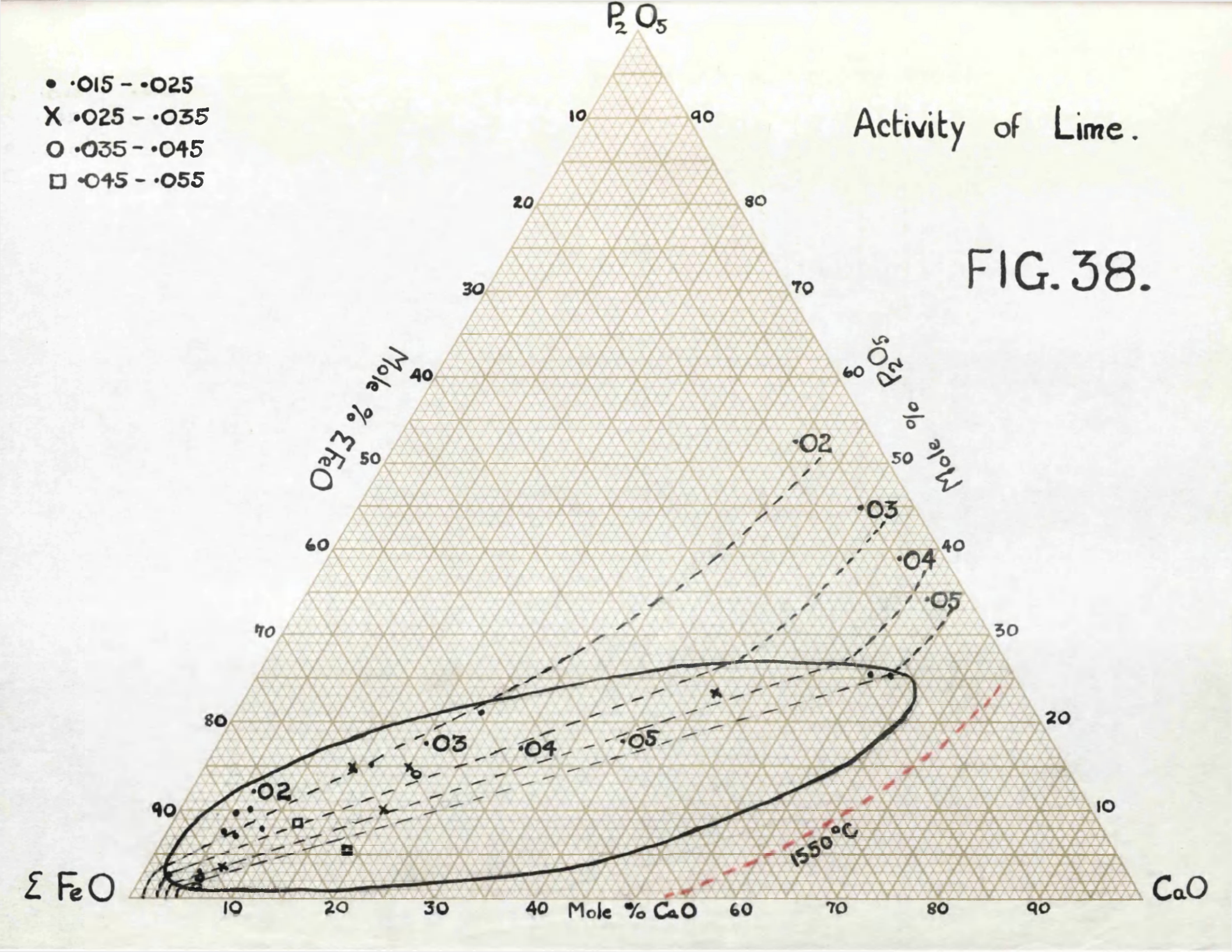


FIG. 37.

better with the $a_{CaO}(3)$ values rather than with those obtained using the free energy equation of Richardson, Jeffes and Withers(72), ($a_{CaO}(4)$), thereby suggesting that the free energy equation used to derive $a_{CaO}(3)$, is the more correct. Values of $a_{CaO}(3)$ have therefore been plotted against composition in the ternary diagram shown in Figure 38, which also shows the approximate solubility curve for lime at 1550°C, based on the results of Fischer and vom Ende(40) and Oelsen and Maetz(15). This curve corresponds to unit lime activity. It is obvious then, that a very rapid drop in lime activity occurs over a relatively small composition range, due to the marked effect of phosphorus pentoxide on the activity of lime. Conversely, Figure 34 shows the similar effect of lime on the activity of phosphorus pentoxide in the slag.


• ·015 – ·025
X ·025 – ·035
O ·035 – ·045
□ ·045 – ·055
Activity of Lime.
FIG. 38.
P2 O5
Mole % ΣFeO
Mole % P2O5
Σ FeO
CaO
Mole % CaO
·02
·03
·04
·05
1550°C
10
20
30
40
50
60
70
80
90

CHAPTER 4.

Slag-Metal Relationships.

Because of the somewhat acid nature of the slags encountered in the present work, few of the equations which have been put forward to interpret phosphorus distribution between slag and metal could be applied to the results obtained here. Thus the relationships of Schenck and Riess(33) and Quarrell and co-workers(35) can only be used with slags of higher basicity. For the same reason the equation of Winkler and Chipman (37) can only be applied to certain of the lower layer compositions. The results so obtained are given in Table 9, where

$$K_P = \frac{4CaO.P_2O_5}{[\%P]^2[\%O]^5(CaO')^4}$$

as defined earlier on page 45.

For the same temperature (1550°C) Winkler and Chipman obtained a value of 10.58 for log K_P. For the slags in Table 9, the main contribution to the mole fraction of "CaO'" was made by magnesia. It is clear that magnesia cannot be regarded as being equivalent to lime in dephosphorisation. Winkler and Chipman obtained even lower values for log Kp when lime was largely replaced by manganous oxide, and similarly attributed this to the poorer dephosphorising power of manganous oxide.

The more general relationships of Turkdogan and Pearson(45) and Flood and Grjotheim(44) are applicable to all the present data. A comparison of the results of the present work with the equation of the former workers is shown in Figure 39. The straight line represents their equation:

$$\log \gamma_{P_2O_5} = -1{\cdot}12 \Sigma AiNi - \frac{42{,}000}{T} + 23{\cdot}56$$

TABLE 9.

Run No.	log K_p
9	6.92
13	8.09
14	7.50
16	7.03
18	8.15
23	6.90
24	7.67
31	7.23
32	7.18
37	8.39
38	7.53
39	7.09
40	6.39

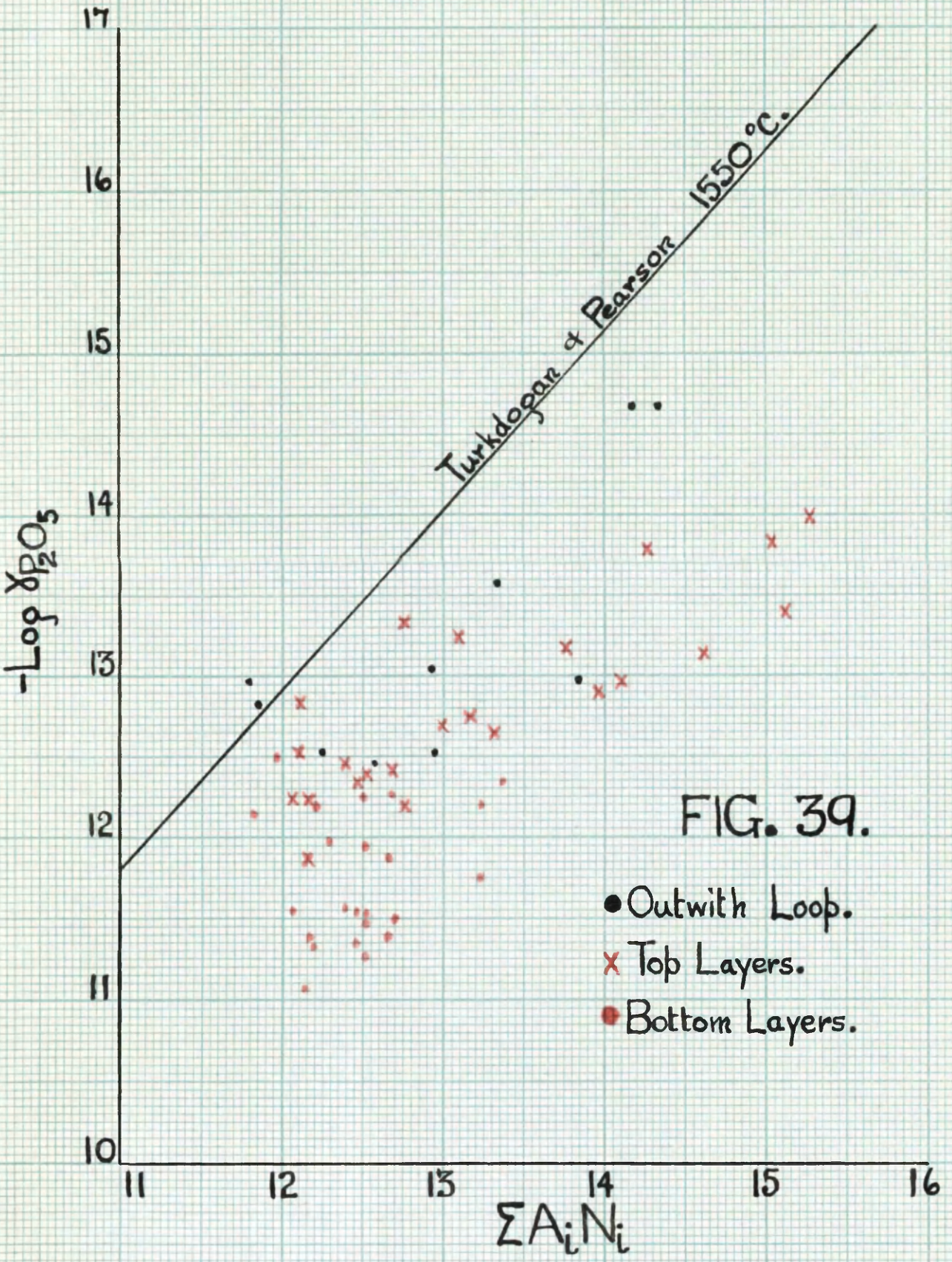

17
16
15
14
13
12
11
10
11
12
13
14
15
16
$-\text{Log } \gamma_{P_2O_5}$
$\Sigma A_i N_i$
Turkdogan & Pearson 1550°C.
Outwith Loop.
Top Layers.
Bottom Layers.

FIG. 39.

calculated for 1550°C. Values of log $\gamma_{P_2O_5}$ for the present work were derived from the mole fractions and activities of phosphorus pentoxide in the slag given in Table 6. It will be seen that agreement with the relationship of Turkdogan and Pearson is poor. Their equation showed equally unsatisfactory agreement with the results of Winkler and Chipman. This was ascribed to the fact that the slags used by the latter authors were neutral in character, the equation used being regarded as only applicable to basic slags of the type used in basic steelmaking.

The equation of Flood and Grjotheim(44) was derived from a consideration of the slag-metal data of Winkler and Chipman for 1570-1638°C (i.e., an average temperature of 1600°C). Since the present work was carried out at 1550°C., the same procedure was used to derive values of log $K'_{Ca^{++}}$ and log $K'_{Fe^{++}}$ at this temperature, i.e., values of log K_{obs} were plotted against $N_{Ca^{++}}$ and $N_{Fe^{++}}$ as shown in Figures 40 and 41, and extrapolated to $N_{Ca^{++}} = 1$ and $N_{Fe^{++}} = 1$ respectively.

It will be seen that there is a considerable scatter of the points in Figures 40 and 41. There is, however, no reason to expect all the experimental points to lie on a single curve because the plot does not take into account changes in the concentration of the other cations present in the slag. Thus in Figure 40 it can be seen that the points corresponding to top layer compositions approximate to a straight line. Compositions lying outside the immiscibility gap show higher values of log K_{obs}, whereas bottom layer compositions give rise to lower values. This is because compositions lying outside the gap contain more magnesia fluxed from the crucible, than do those compositions within the immiscibility

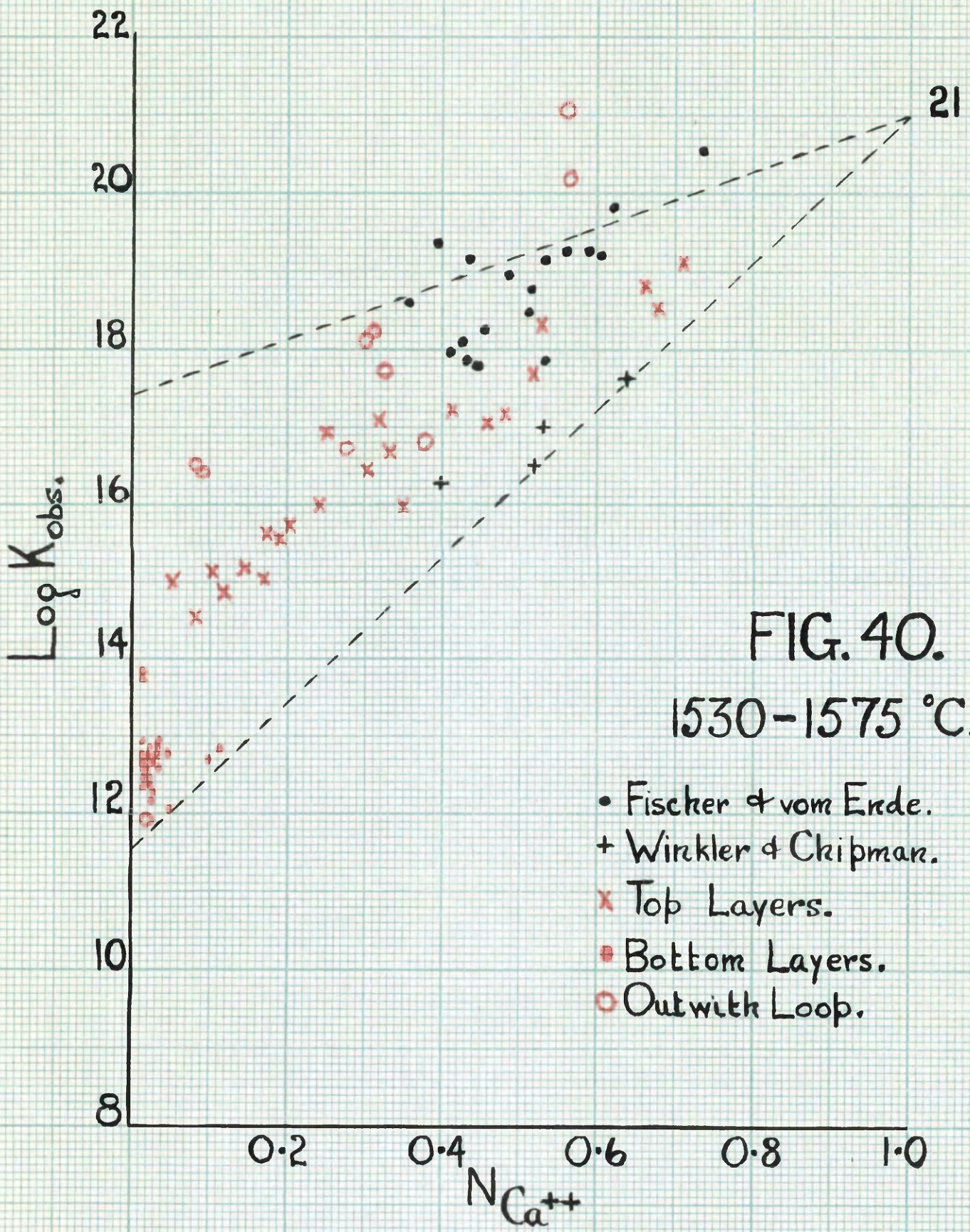


FIG. 40.

1530-1575 °C.

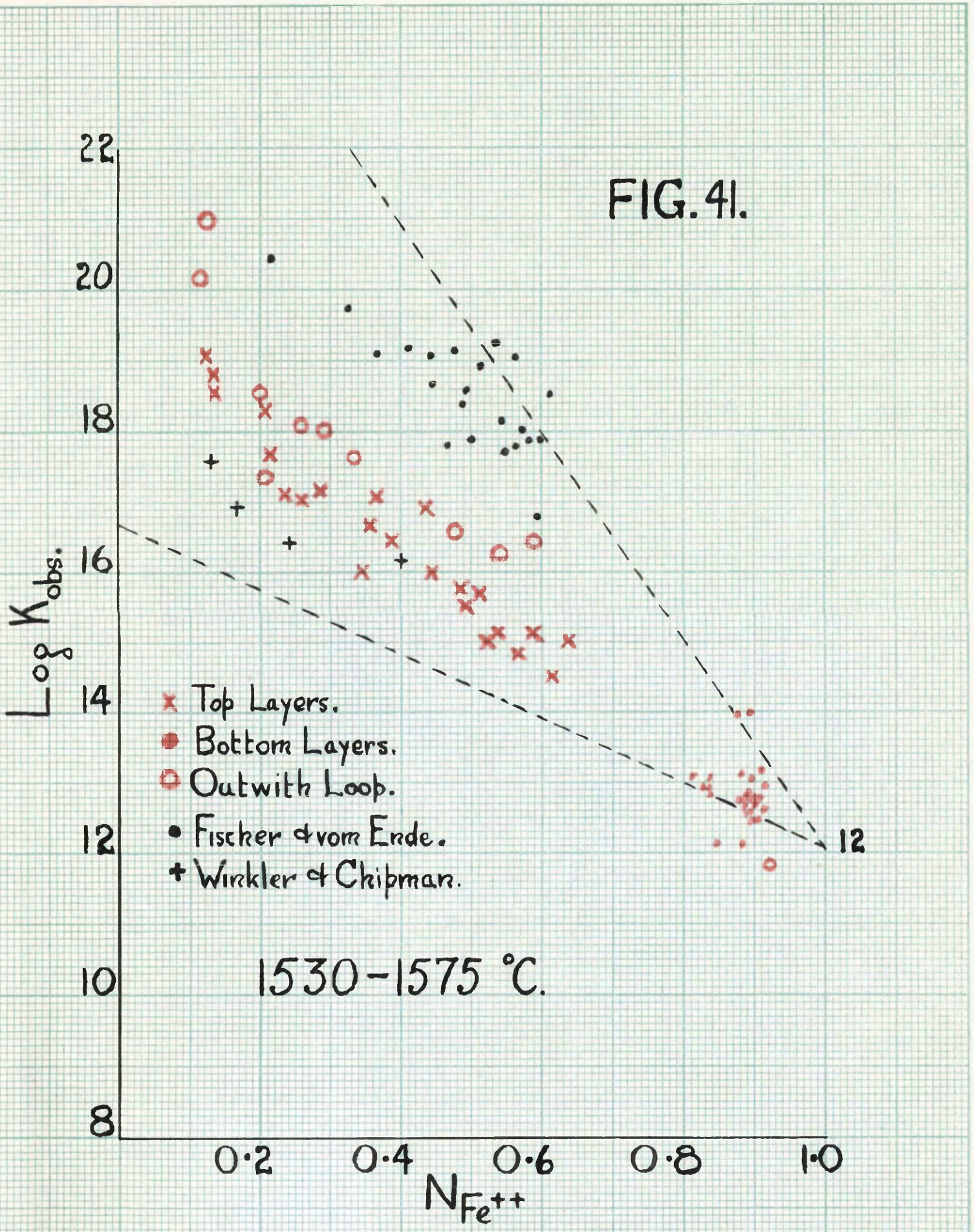


FIG. 41.
22
20
18
16
14
12
10
8
Log $K_{obs.}$
× Top Layers.
● Bottom Layers.
○ Outwith Loop.
• Fischer & vom Ende.
+ Winkler & Chipman.
1530-1575 °C.
12
0·2
0·4
0·6
0·8
1·0
$N_{Fe^{++}}$

gap. Since the presence of larger quantities of magnesia must be accompanied by lower ferrous oxide concentrations, and magnesium orthophosphate is more stable than ferrous orthophosphate, a higher value of log K_{obs} results. Similarly, since the lower layer compositions contain large percentages of iron oxide and only small amounts of magnesia, log K_{obs} is low. In the same way the values obtained from Winkler and Chipman's complex slags are generally low. The relatively pure lime-saturated slags of Fischer and vom Ende give higher values than expected. The scatter must narrow, however, as a mole fraction of unity is approached on account of the small changes permissible in the remaining cation concentrations.

The extrapolated values of log K'_{Ca++} and log K'_{Fe++} obtained, however, would be expected to be slightly different from those given by Flood and Grjotheim, as the latter authors assumed ferric iron was present as $(FeO_4)^{5-}$, whereas in the above calculations all the iron has been expressed as Σ FeO. This method has been adopted for the following reasons:-

1. Due to the sampling technique used in the present investigation, there existed the possibility of oxidation of the chilled slag on cooling.
2. For compositions lying within the immiscibility gap, only approximate values for the ferric oxide content of each layer could be obtained.
3. Uncertainty still exists as to the state of ionisation of ferric iron in liquid slags.

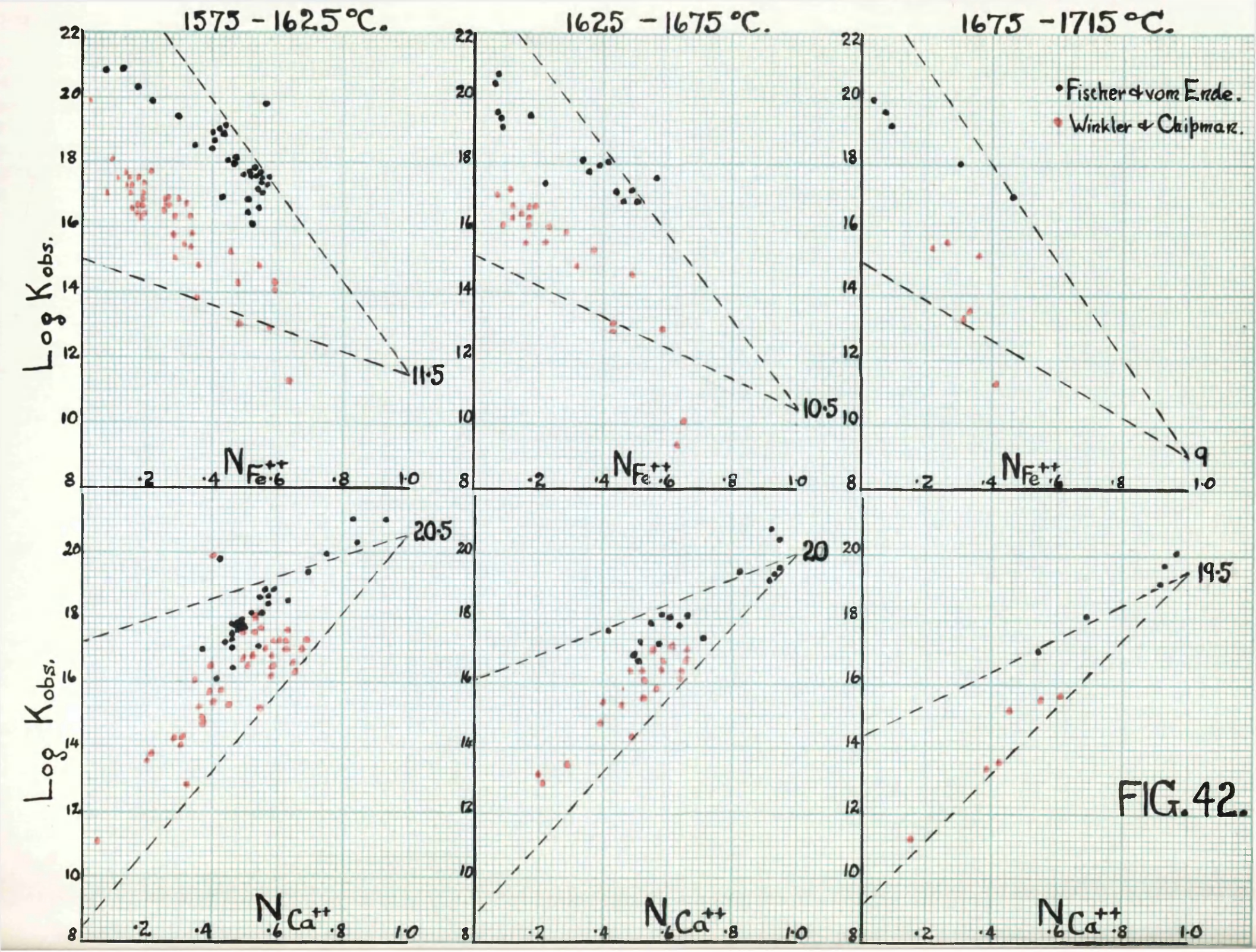

1575 - 1625 °C.
1625 - 1675 °C.
1675 - 1715 °C.
Log $K_{obs.}$
$N_{Fe^{++}}$
$N_{Ca^{++}}$
11·5
10·5
9
20·5
20
19·5
• Fischer & vom Ende.
• Winkler & Chipman.

FIG. 42.

Log K'_{Mg++} and log K'_{Mn++} were derived by the same method as was used by Flood and Grjotheim, i.e., by obtaining values which gave the best fit with the experimental data.

As the phosphorus reaction is strongly temperature dependent, an effort has been made to obtain further log K'_{M++} values (where M = Ca, Mg, Mn, Fe) at other temperatures. The data of Winkler and Chipman and Fischer and vom Ende, for the temperature ranges, 1575-1625, 1625-1675 and 1675-1715°C, were used for this purpose as shown in Figure 42. The log K'_{M++} values obtained are summarised in Table 10.

The values of log K'_{M++} given in Table 10 have been plotted against the reciprocal of the absolute temperature in Figure 43. Although an equation for the free energy change for the reaction

$$2[P] + 5[O] + 3(O^{=})_{(M++)} \longrightarrow 2(PO_4^{\equiv})_{(M++)}$$

for each of the ions concerned could be calculated from the relationships depicted in Figure 43, this has not been done as very slight changes in the estimated slopes of the lines cause very large changes in the individual ΔH and ΔS terms, and little reliance could be placed on their absolute values.

Values of log Kp have been calculated from the data given in Table 10 for the slag-metal results obtained in the present work, and recorded in Table 11, along with the corresponding observed values. The comparison is shown graphically in Figure 44 which also includes results of similar calculations for the data of Winkler and Chipman covering the temperature range 1550-1715°C.

TABLE 10.

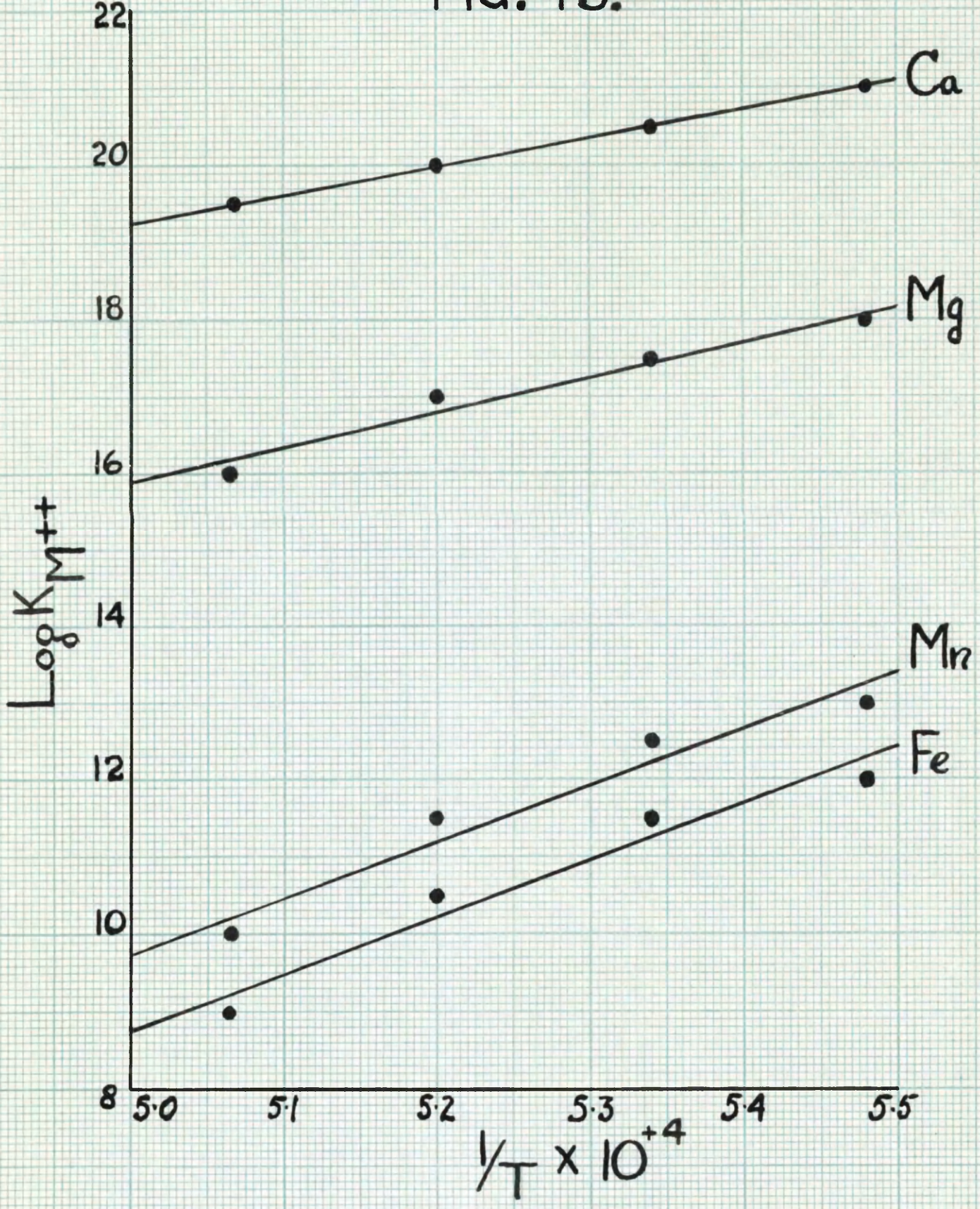
Temperature °C.	log K'_{Ca++}	log K'_{Mg++}	log K'_{Mn++}	log K'_{Fe++}
1550	21.0	18	13	12
1600	20.5	17.5	12.5	11.5
1650	20.0	17	11.5	10.5
1700	19.5	16	10.0	9.0

TABLE 11.

Run No.	Top Layers.		Bottom Layers.	
	$\log K_{calc.}$	$\log K_{obs.}$	$\log K_{calc.}$	$\log K_{obs.}$
6	15.44	15.67	12.56	12.80
8	14.58	14.51	12.60	12.55
9	16.99	15.96	12.70	12.14
10	15.21	15.18	12.58	12.43
12	14.35	15.00	12.75	12.79
13	16.76	17.11	12.67	12.92
14	16.84	16.67	12.68	12.44
16	19.21	18.57	13.16	12.71
18	18.03	17.17	12.81	11.96
19	14.76	15.12	12.65	12.92
23	16.05	15.95	12.67	12.21
24	16.60	16.45	12.68	12.50
28	16.16	16.93	12.63	13.86
31	19.20	18.83	13.29	12.70
32	19.37	19.07	13.44	12.84
36	15.70	15.72	12.73	12.59
37	18.33	18.32	13.07	12.78
38	18.26	17.69	13.00	12.01
39	17.53	17.16	12.70	12.75
40	17.83	17.05	12.76	12.29
41.	15.62	15.66	12.73	12.61
42	15.39	15.05	12.73	12.52
43	14.95	14.86	12.67	12.35

Run No.	Outwith Loop.	
	$\log K_{calc.}$	$\log K_{obs.}$
3	17.93	18.37
4	17.93	17.13
5	16.98	17.53
7	14.65	16.23
11	12.58	11.75
22	17.14	17.94
26	18.91	20.78
27	19.18	19.97
30	14.99	16.03
35	17.38	17.87

FIG. 43.


22
20
18
16
14
12
10
8
Log $K_{M^{++}}$
Ca
Mg
Mn
Fe
5·0
5·1
5·2
5·3
5·4
5·5
$1/T \times 10^{+4}$

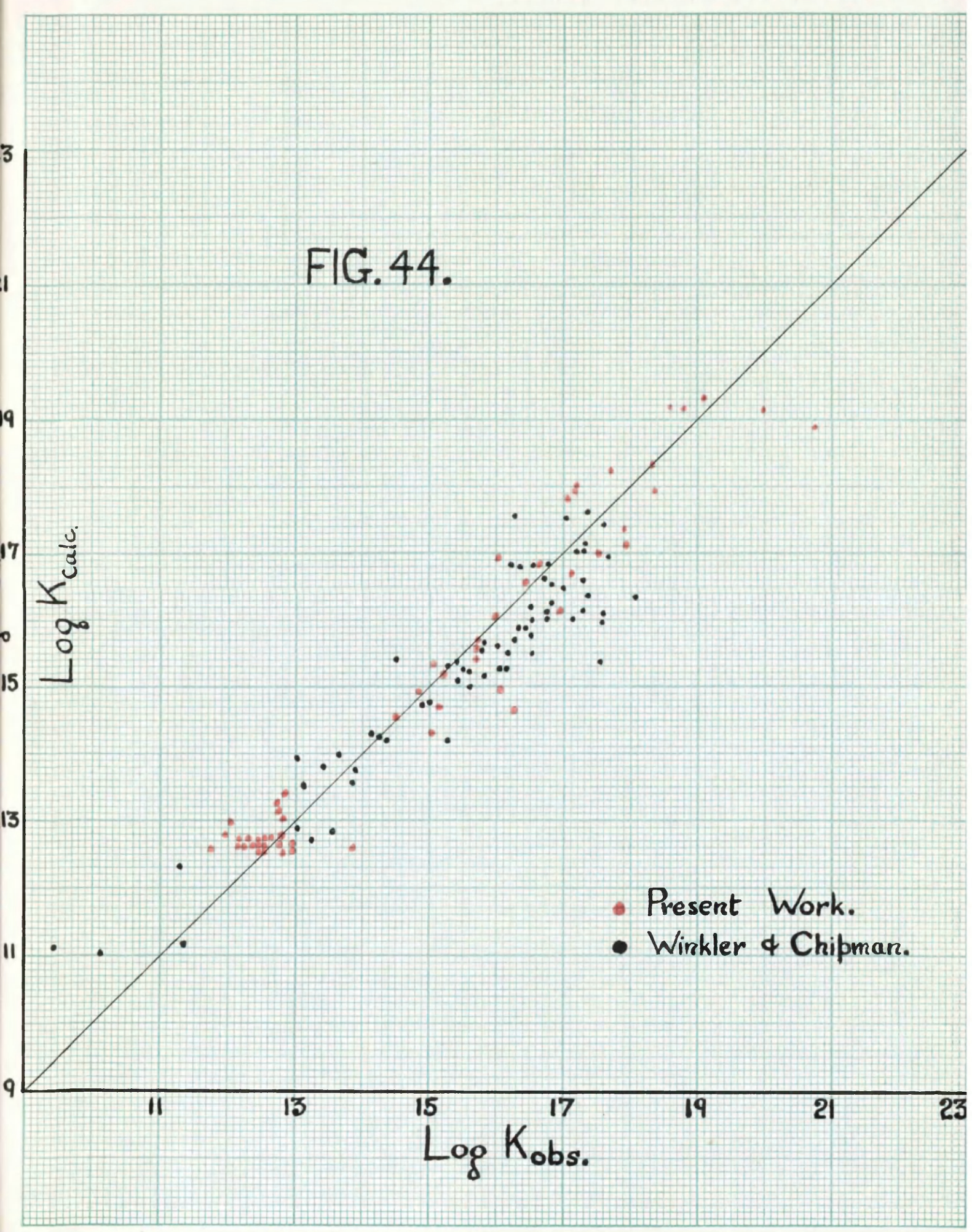


FIG. 44.
Log $K_{calc.}$
Log $K_{obs.}$
Present Work.
Winkler & Chipman.
9
11
13
15
17
19
21
23

Figure 45 shows a similar comparison for Fischer and vom Ende's data for a similar temperature range. It will be seen that agreement between calculated and observed values is poor, and that the observed values are considerably higher than the corresponding calculated values.

It seems probable that the slags used by Fischer and vom Ende would contain high percentages of ferric oxide, combined in the form of calcium ferrites, and that the contribution of ferrous ions to log $K_{calc.}$ has been overestimated. In consequence the contribution of calcium ions has been underestimated. If proper allowance had been made for the ferric oxide content in their slags it is probable that the investigations of Fischer and vom Ende would have fallen in line with those of Winkler and Chipman, and the present work. The equation of Turkdogan and Pearson was largely based on data obtained using more basic slags, than those used in the present investigation. As these would be expected to contain higher proportions of ferric iron the discrepancy shown in Figure 39, between the present results and the equation of Turkdogan and Pearson would be expected to be reduced if appropriate allowance were made for the effect of ferric iron. Further work using the present procedure but with more basic slags would require to be carried out to show whether this was the only reason for the observed discrepancy.

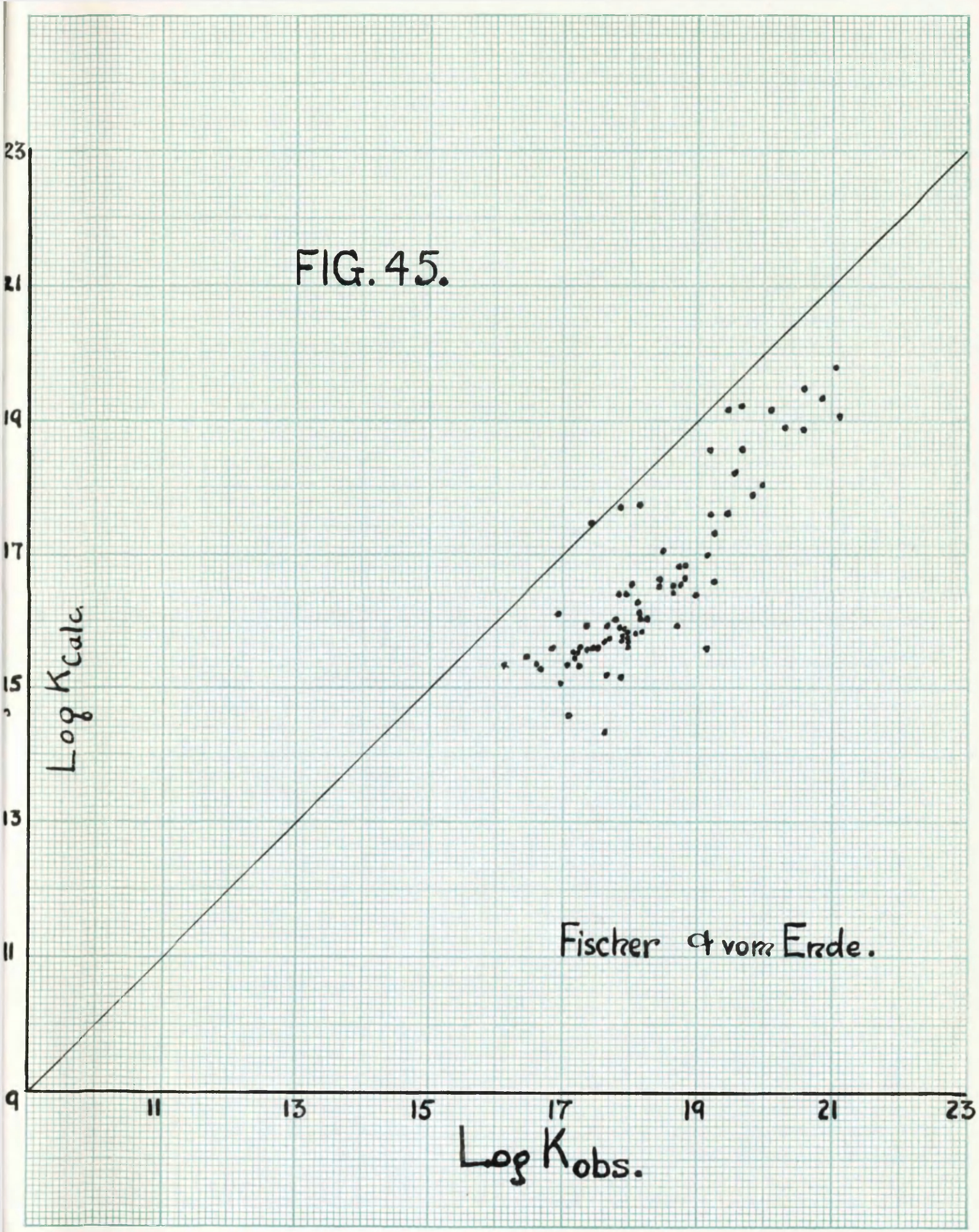


FIG. 45.
Log $K_{calc.}$
Log $K_{obs.}$
23
21
19
17
15
13
11
9
11
13
15
17
19
21
23
Fischer & vom Erde.

APPENDIX.

Influence of Phosphorus on the Solubility of Nitrogen in Molten Iron at 1550°C.

Although a knowledge of the solubility of gases is of considerable practical importance, the effects of alloying elements on their solubility in molten iron have only been studied to a limited extent. One of the earliest investigations on the solubility of nitrogen in pure iron was carried out by Sieverts(73) who reported its solubility at 1550°C under one atmosphere pressure to be 0·039 per cent. This figure was later confirmed by Chipman and Murphy(74). Experimental data on the effect of various alloying elements on the solubility of nitrogen at one atmosphere pressure in iron at 1600°C are reproduced in Figure 46. In this graph it can be seen that chromium and vanadium(75) and to a lesser extent manganese(76) cause a marked increase in the nitrogen solubility, while carbon(77) has a lowering effect, and silicon (78), after an initial increase, likewise reduces the solubility. No data has been published, however, on the effect of phosphorus or oxygen on nitrogen solubility, although the slag-metal experiments carried out by Bell(79) have shown that, in the presence of small concentrations of manganese and silicon, oxygen reduces the solubility of nitrogen in molten iron.

The analysed concentrations of phosphorus and nitrogen shown in Table 5 are plotted in Fig.47, where it can be seen that phosphorus has little effect on the solubility of nitrogen in iron. There may be a very slight increase in solubility with increasing phosphorus content.

The scatter is similar to that obtained by other workers, and may be attributed to the small weight of sample used in the vacuum fusion determinations.

A marked increase in nitrogen solubility, with alloy concentration may be regarded as a measure of stability of the nitride of the alloying element. This is reflected in the curves in Figure 46 for chromium and vanadium - both of which are known to form nitrides, which are stable in molten iron. Unfortunately no data are available on the stability of phosphorus nitride(s) at high temperatures, but from the gradient of the line drawn in Figure 47, it would seem that its stability is very much lower than that of chromium or vanadium nitride.

Since the nitrogen solubility is also affected by the oxygen concentration in the metal, the lowering effect of oxygen should be taken into account before drawing any conclusions concerning the influence of phosphorus alone. In the case of the present data, however, there seems, from Figure 36, to be little dependence of phosphorus on the oxygen concentration in the metal, so that the resulting variations in nitrogen solubility caused by dissolved oxygen, will be spread over the whole phosphorus concentration range plotted in Figure 47. Such a correction would have the effect of producing a scatter of points, the best line through which would have the same gradient as in Figure 47, but at a higher nitrogen solubility level.

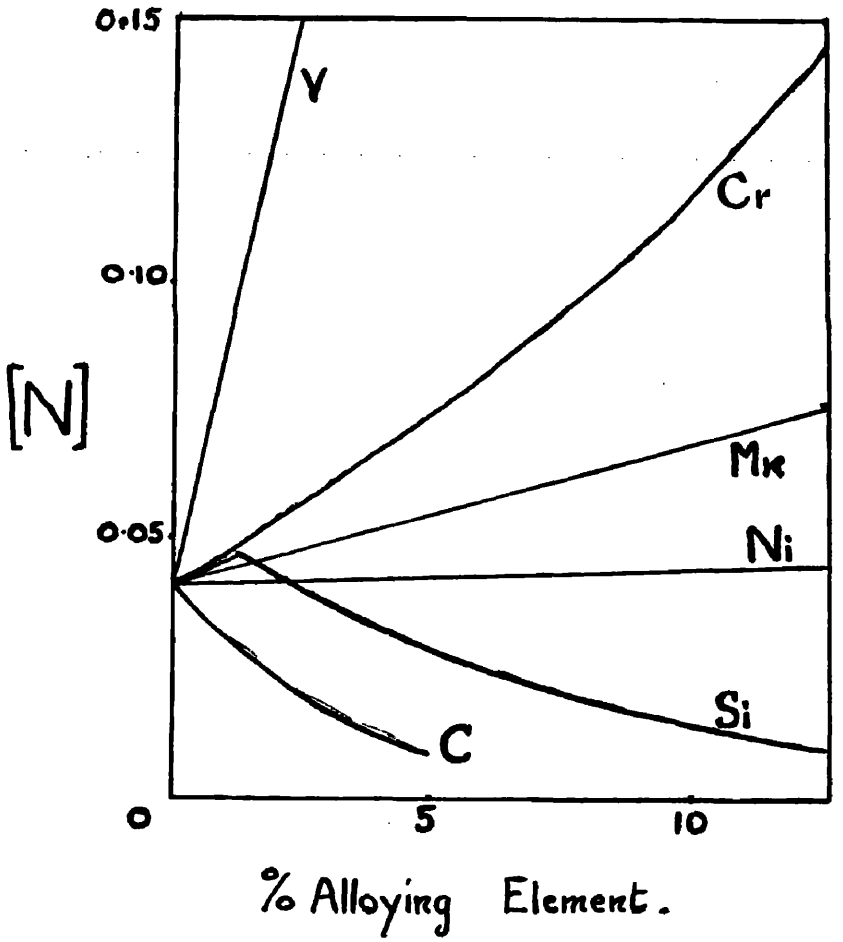


FIG. 46.

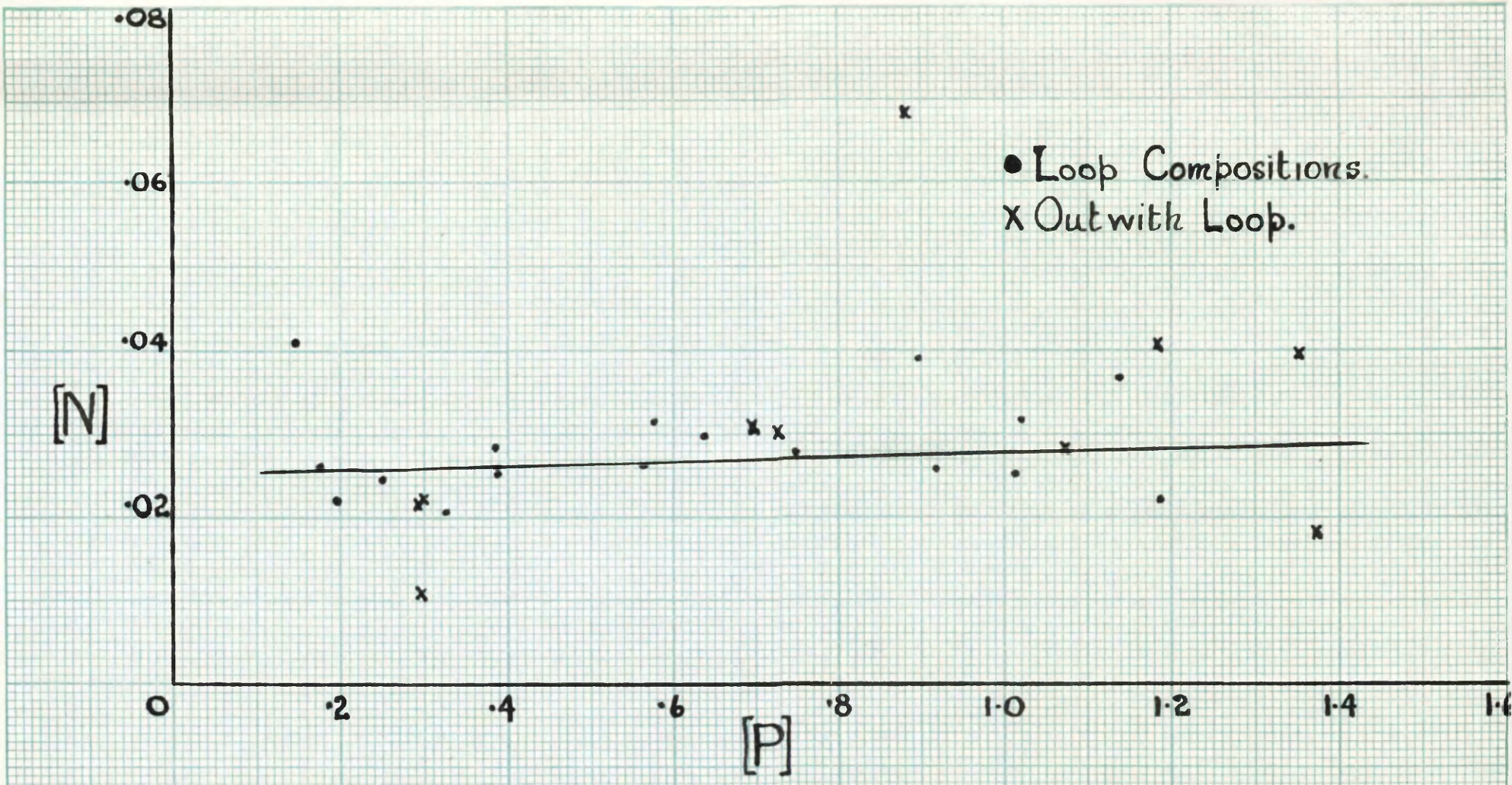


FIG. 47.

At higher phosphorus concentrations, however, it is probable that the curve will attain a maximum value, followed by a lowering in nitrogen solubility caused by the reducing effect of phosphorus on the activity of iron, through the formation of iron phosphides. A similar observation was made by Vaughan and Chipman(78) in their work on the effect of silicon on nitrogen solubility in molten iron.

CONCLUSIONS.

The following are the main conclusions reached in the present work:-

1. The $FeO-3FeO.P_2O_5$ "binary" system is eutectiferous, with a eutectic at 930°C and 30 pct. P_2O_5. The melting point of $3FeO.P_2O_5$ was redetermined as 1020°C.

2. The existence of an immiscibility gap in the $CaO-FeO-P_2O_5$ system has been confirmed, and its limits determined at the liquidus temperature and at 1550°C. In the $FeO-3FeO.P_2O_5-3CaO.P_2O_5$ section of this system, a binary eutectic solidification curve of wustite and a $3(Fe,Ca)O.P_2O_5$ solid solution was found to pass through the immiscibility gap. No evidence was obtained for a ternary eutectic in this partial system.

3. The results of slag-metal equilibrium experiments have been used to determine a_{FeO}, a_{CaO} and $a_{P_2O_5}$ in $CaO(MgO)-FeO-P_2O_5$ slags. The presence of the immiscibility gap causes large positive deviations from ideality in the case of FeO. The isoactivity curves for CaO and P_2O_5 show that each has a pronounced lowering effect on the activity of the other.

4. The present results have been shown to be consistent with an ionic interpretation of slag constitution. Apparent discrepancies in the data of certain workers can be attributed to the presence of ferric iron in the slags. The effect of temperature on the phosphorus equilibrium between slag and metal has been determined.

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